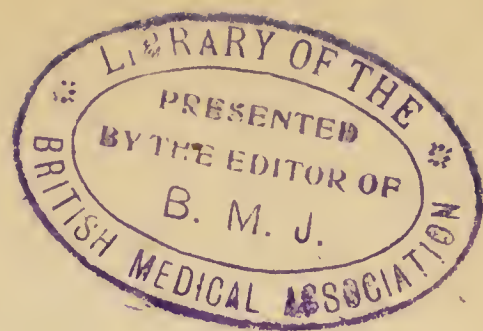


145 H



22102074223

Med
K2003



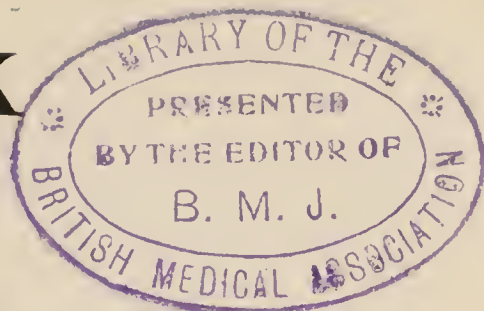


Digitized by the Internet Archive
in 2019 with funding from
Wellcome Library

<https://archive.org/details/b31357751>

11/10/19. 20/- 142

TEXT-BOOK
OF
CHEMISTRY



INORGANIC AND ORGANIC
WITH TOXICOLOGY

FOR STUDENTS OF MEDICINE, PHARMACY,
DENTISTRY AND BIOLOGY

BY

R. A. WITTHAUS, A.M., M.D.

LATE PROFESSOR OF CHEMISTRY, PHYSICS AND TOXICOLOGY IN CORNELL UNIVERSITY

Seventh, Revised Edition

BY

R. J. E. SCOTT, M.A., B.C.L., M.D.

FELLOW OF THE NEW YORK ACADEMY OF MEDICINE: EDITOR OF "WITTHAUS' ESSENTIALS
OF CHEMISTRY AND TOXICOLOGY," ETC., ETC.

LONDON :

JOHN BALE, SONS & DANIELSSON, Ltd.

OXFORD HOUSE

83-91, GREAT TITCHFIELD STREET, OXFORD STREET, W.

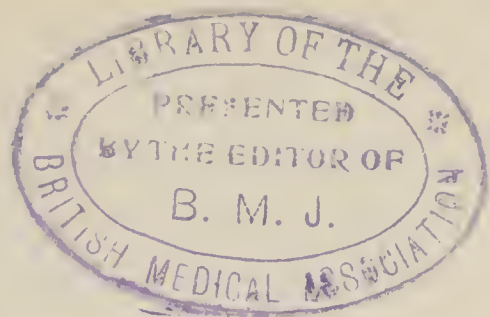
1919

19 346 448.

COPYRIGHT, 1919
BY WILLIAM WOOD AND COMPANY

WELLCOME INSTITUTE LIBRARY	
Coll.	welMOrnec
Call	
No.	QD

PRINTED IN NEW YORK
BY WILLIAM WOOD AND COMPANY



PREFACE

In the preface to the earlier editions of this book the author clearly specified its scope and purpose. The general plan of the work remains unaltered, and may be indicated by the following extracts from the preface to the sixth edition.

“ The main purpose of the section on inorganic chemistry is to supply certain data which shall serve as the text upon which to discuss the general principles of chemistry. It is the opinion of the author that the object of chemical teaching should not be to lay up in the memory of the student a store of isolated facts, but rather to train his mind in those general principles by which he may reason out chemical problems for himself. If a teacher of chemistry to medical students aim merely to supply them with chemical facts, he and they are fore-ordained to disappointment, but if the student be led to ‘ think in chemistry,’ the success and possible extent of the teaching, both in the fundamentals and in the superstructure of organic and physiological chemistry, which can be attained, will be surprising and delightful to both instructor and pupil. And in this connection it must be said that the order of consideration of the several subjects which has been here followed, because it is logical, is not recommended in the teaching of students. The study should begin with that of a few elements and compounds, the consideration of the general physical and chemical principles being taken up as material for their discussion is supplied.

“ The section on organic chemistry has been rearranged in the light of further information upon the relationship of substances, and somewhat extended, the prominence given to this branch of the subject the author believes to be justified, notwithstanding its intricacy and the impossibility of teaching it satisfactorily to those not well grounded in general chemistry, because of the intimate connection of organic chemistry with physiology and with modern pharmacy, and the impossibility of the comprehension of the problems of animal and pharmaceutical chemistry without the possession of an adequate knowledge of the principles of organic chemistry.”

Since the first edition of this book appeared, and particularly since the death of its distinguished author, many changes have occurred in the medical curriculum; and not the least of these pertain to the

subject of chemistry. Inorganic chemistry and the principles of organic chemistry are now generally presumed to have been mastered in the preparatory schools, and their study is reviewed and amplified in the first year of the medical course as preliminary to the important (special) subject of physiological chemistry.

The book is still intended mainly for medical students, and the present revision has been made with the purpose of providing a work which shall be suitable for students in the preparatory and scientific schools, and which may also serve as a text-book for the medical or professional student throughout his college course.

During the process of revision the main difficulty has been to prevent the book from becoming of unreasonable size. Many of the sections on Physics have been omitted, it being presumed that the student possesses, and has studied, a text-book on that subject. The part dealing with Physiological Chemistry is omitted, because the subject is now of such importance and of such dimensions that its study is more advantageously made from special text-books, of which there are now many excellent ones available. Such of the organic chemistry as could be spared has also been left out, and further space has been gained by printing in smaller type the sections on toxicology and some of the less important general topics. The equations have been printed each on a line by itself, so as to make the subject clearer and more attractive to the beginner. Care has been taken not to make the book (particularly the part dealing with Organic chemistry) a mere catalogue of names and formulæ.

New material has been added where it was considered necessary, and care has been taken to present and emphasize general principles rather than isolated facts. In several of the sections of the organic chemistry equations showing the Grignard reactions have been freely introduced. Many of the new paragraphs were indicated by the late Professor Witthaus as desirable, and, in some cases they have been taken from his manuscript notes.

R. J. E. SCOTT.

New York.

September, 1918.



TABLE OF CONTENTS

INTRODUCTORY—GENERAL CHEMISTRY

	PAGE
Matter—Force—Chemistry	1
General Properties of Matter:	
Indestructibility—Impenetrability—Divisibility—Inertia —Weight — Apparent Weight — Energy — Specific Weight—Density—Pressures—States of Matter— Cohesion	2
Special Properties of Solids, Liquids and Gases.....	4
Crystallization—Allotropy — Diffusion — Boyle-Mariotte Law—Absorption of Gases	4
Some Physical Actions of Chemical Interest	11
HEAT:	
Temperature — Thermometers — Thermal Unit — Changes in Volume—Dalton-GayLussac Law— Law of Charles—Absolute Temperature—Change of State—Fusion — Latent Heat—Solution — Congelation—Vaporization—Gases and Vapors —Boiling—Liquefaction — Distillation — Subli- mation—Specific Heat	11
ELECTRICITY:	
Insulators—Conductors—Ions—Galvanic Electricity —Electromotive Force—Resistance—Ohm's Law —Electrolysis—Electrical Units.....	17
Chemical Phenomena	21
Elements—Compounds—Mixtures—Laws Governing the Combination of Elements—Molecular and Atomic Theories—Atomic Weight—Molecular Weight—Mol —Molecular Volume—Valence—Symbols, Formulæ and Equations—Electrolysis—Acids, Bases and Salts —Concentration — Stoichiometry — Nomenclature— Radicals—Composition and Constitution—Chemical Energy—Chemical Equilibrium—Reversible Re- actions—Mass Action—Chemical Effects of Light— Classification of Elements—Periodic Law.....	21

INORGANIC CHEMISTRY

	PAGE
Typical Elements	57
Hydrogen	57
Oxygen—Ozone	59
Compounds of Hydrogen and Oxygen: Water— —Natural Waters—Hydrogen Dioxide.....	62
Elements which form no Compounds	72
Helium—Neon—Argon—Krypton—Xenon—Niton	72
Acidulous Elements	73
CHLORINE GROUP	73
Fluorine and its Compounds	73
Chlorine and its Compounds	74
Bromine and its Compounds	80
Iodine and its Compounds	81
SULPHUR GROUP	83
Sulphur and its Compounds	84
Selenium and Tellurium	93
NITROGEN GROUP	93
Nitrogen and its Compounds—Atmospheric Air	94
Phosphorus and its Compounds	103
Arsenic and its Compounds	110
Antimony and its Compounds	120
BORON GROUP	123
Boron and its Compounds	123
CARBON GROUP	124
Carbon	124
Silicon and its Compounds	127
VANADIUM GROUP	128
Vanadium—Columbium—Tantalum	128
MOLYBDENUM GROUP	128
Molybdenum—Tungsten—Osmium	128
Amphoteric Elements	129
GOLD GROUP	129
Gold and its Compounds	129
IRON GROUP	130
Chromium and its Compounds	130
Manganese and its Compounds	131
Iron and its Compounds	132

	PAGE
URANIUM GROUP	137
Uranium and its Compounds	137
LEAD GROUP	138
Lead and its Compounds	138
BISMUTH GROUP	142
Bismuth and its Compounds	142
TIN GROUP	144
Titanium	145
Zirconium	145
Tin and its Compounds	145
PLATINUM GROUP	147
Palladium—Platinum and its Compounds	147
RHODIUM GROUP	147
Rhodium—Ruthenium—Iridium	147
Basylous Elements	149
SODIUM GROUP	149
Lithium and its Compounds	149
Sodium and its Compounds	151
Potassium and its Compounds	156
Cæsium—Rubidium	163
Silver and its Compounds	164
Ammonium Compounds	165
THALLIUM GROUP	168
Thallium	168
CALCIUM GROUP	168
Calcium and its Compounds	168
Strontium and its Compounds	171
Barium and its Compounds	171
MAGNESIUM GROUP	172
Magnesium and its Compounds	173
Zinc and its Compounds	175
Cadmium	177
ALUMINIUM GROUP	177
Glucinum—Scandium—Gallium—Indium	177
Aluminium and its Compounds	178
NICKEL GROUP	180
Nickel and its Compounds	180
Cobalt	181
COPPER GROUP	181
Copper and its Compounds	181
Mercury and its Compounds	184

ORGANIC CHEMISTRY

PAGE

Compounds of Carbon:

Organic Chemistry—Homologous Series—Isomerism— Elementary Organic Analysis—Determination of Mo- lecular Weights—Determination of Constitution— Characterizing Groups—Nomenclature — Classifica- tion of Carbon Compounds	191
--	-----

Open Chain, Aliphatic, Acyclic, or Fatty Compounds.....	201
Hydrocarbons	201
Saturated Compounds—Methane Series	201
Hydrocarbons	202
Haloid Derivatives	204
Oxidation Products	208
Alcohols	210
Aldehydes and Ketones	225
Carbohydrates	235
Carboxylic Acids	250
Alcohol-acids—Oxyacids	259
Aldehyde-acids	265
Ketone-acids	266
Oxyaldehyde and Oxyketone Acids	266
Simple ethers	267
Acid Anhydrides	269
Acidyl Halides	270
Oxides of Carbon	270
Esters—Compound Ethers	275
Sulphur Derivatives of the Paraffins	284
Organo-metallic Compounds	288
Nitrogen Derivatives of the Paraffins	291
Nitroparaffins	292
Amines and Ammonium Derivatives	292
Oxyamines—Hydramines—Diamines	296
Amidines—Amidoximes—Hydroxamic Acids ...	300
Guanidine and its Derivatives	301
Hydrazines—Hydrazides	302
Nitriles—Cyanogen Compounds	303
Amides	310
Thiourea and Thiocarbamic Acids	316
Compound Ureas	316

	PAGE
Nitrogen Derivatives of Alcohols, Aldehydes and Ketones	319
Nitrogen Derivatives of Acids	321
Phosphorus, Antimony and Arsenic Derivatives	326
Unsaturated Aliphatic Compounds	327
Hydrocarbons	327
Oxidation Products	330
Sulphur and Nitrogen Compounds	333
Closed Chain, Aromatic, or Cyclic Compounds	334
Carbocyclic Compounds	335
Hexacarbocyclic Compounds—Aromatic Substances	336
Monobenzenic Compounds	341
Hydrocarbons	341
Haloid Derivatives	343
Phenols	344
Quinones	350
Aromatic alcohols	351
Alphenols	352
Aldehydes	353
Ketones	354
Aromatic Carboxylic Acids	355
Phenol Carboxylic Acids and their Esters.....	357
Phenylic Ethers—Glucosides	360
Anhydrides and Acid Halides	364
Aromatic Sulphur Derivatives—Sulphonic Acids	365
Nitrogen-containing Derivatives of Benzene....	367
Hydroaromatic Compounds with a Single Nucleus..	381
Hydrocarbons	381
Hydroaromatic alcohols	382
Hydroaromatic Ketones and Acids.....	383
Compounds with Condensed Nuclei	385
Condensed Hydrocarbons	386
Phenols—Quinones	386
Diphenyl and its Derivatives	388
Diphenyl Paraffins—Diphenyl Olefines—Diphenyl Acetylenes	388
Phenols—Alcohols	389
Heterocyclic Compounds	389
Mononucleate Heterocyclic Compounds	391
Five-membered rings	391
Six-membered rings	396

	PAGE
Condensed Heterocyclic Compounds	414
Condensed Nuclei Containing a Nitrogen Member	415
Alkaloids	419
Ptomaines, Leucomaines and Toxines	442
APPENDIX	445
INDEX	449

TABLE OF WEIGHTS AND MEASURES

WEIGHTS

1 milligram	= 0.001 gram	= 0.015 grain	Troy.
1 centigram	= 0.01	"	= 0.154 " "
1 decigram	= 0.1	"	= 1.543 grains "
1 GRAM		= 15.432	" "
1 decagram	= 10 grams	= 154.324	" "
1 hectogram	= 100	"	= 0.268 pound "
1 kilogram	= 1000	"	= 2.679 pounds "
	1 grain	= 0.065 gram.	
	1 dram	= 3.888 grams.	
	1 ounce	= 31.103	"
	1 pound	= 373.25	"
1 pound Avoirdupois	= 453.5925 grams.		
1 kilo	= 2.2046 pounds	Avoirdupois.	

MEASURES OF LENGTH

1 millimeter	= 0.001 meter	= 0.0394 inch.
1 centimeter	= 0.01	" = 0.3937 "
1 decimeter	= 0.1	" = 3.9371 inches.
1 METER		= 39.3708 "
1 decameter	= 10 meters	= 32.8089 feet.
1 hectometer	= 100	" = 328.089 "
1 kilometer	= 1000	" = 0.6214 mile.
	1 inch	= 2.54 centimeters.
	1 foot	= 30.48 centimeters.

MEASURES OF CAPACITY

1 milliliter	= 1 c.c.	= 0.001 liter	= 0.0021 U. S. pint.
1 centiliter	= 10	" = 0.01	" = 0.0211 " "
1 deciliter	= 100	" = 0.1	" = 0.2113 " "
1 LITER	= 1000	"	= 1.0567 " quart.
1 decaliter	= 10 liters	= 2.6418	" gallons.
1 hectoliter	= 100	" = 26.418	" "
1 kiloliter	= 1000	" = 264.18	" "

MEASURES OF VOLUME

1 cubic meter	= 1000	liters.
1 cubic centimeter	= 0.001	liter.
1 liter	= 1	cubic decimeter.
1 liter	= 1.0567	quarts.
1 minim	= 0.0614	cubic centimeter.
1 fluid dram	= 3.70	cubic centimeters.
1 cubic centimeter	= 0.061	cubic inch.
1 fluid ounce	= 29.57	cubic centimeters.
1 pint	= 473.11	cubic centimeters.

SIGNS AND ABBREVIATIONS

The figures in parentheses indicate the page upon which the meaning of the sign or abbreviation is described.

[a] _D	=Specific rotary power for sodium light.	m	=Meter.
aq	=Water of crystallization (64).	m	=Meta.
atm	=Atmospheric pressure.	mm	=Millimeter.
b.p.	=Boiling point (16).	M-N	=Molecular normal solution (37).
C	=Asymmetric carbon atom (239).	M.w.	=Molecular weight.
C*	=Asymmetric carbon atom (239).	N	=Normal (38).
cal.	=Gram calorie (12).	N/10	=Tenth normal (38).
cc	=Cubic centimeter.	n	=Index of refraction for sodium light.
c.c.	=Cubic centimeter.	o	=Ortho.
cm	=Centimeter.	p	=Para.
C.P.	=Chemically pure.	ppt.	=Precipitate.
d	=Dextrogyrous (239).	pts.	=Parts.
dil.	=dilute.	R	=A cyclic compound.
d+l	=Racemic (239).	R	=Resistance.
dm	=Decimeter.	r	=Racemic (239).
E	=Electromotive force (20).	sp. gr.	=Specific gravity.
EMF	=Electromotive force (20).	SS	=Standard solution (38).
Eq-N	=Equivalent normal solution (38).	T	=Absolute temperature (13).
f.p.	=Fusing point (14).	t	=Temperature in degrees Centigrade.
gm	=Gram.	U.S.P.	=United States Pharmacopœia.
i	=Racemic (239).	V _m	=Molecular volume (29).
i	=Iso.	V _s	=Specific volume (4).
insol.	=Insoluble.	Δ	=Double linkage.
K	=Rational calorie (12).	λ	=Wave length of light.
kg	=Kilogram.	μ	=Micromillimeter=.001 millimeter.
kg:cal	=Large calorie (12).	+	=Dextrogyrous.
L	=Liter.	—	=Lævogyrous.
i	=Lævogyrous (239).		



TEXT-BOOK OF CHEMISTRY

INTRODUCTORY—GENERAL CHEMISTRY.

Matter and Force.—As we only become cognizant of matter by the action of force upon it, or of force through its effects upon matter, our appreciations of each are so interwoven that each is usually defined in terms of the other. This “argument in a circle” may be avoided by saying that **matter is that which occupies space.**

In popular language the words *matter* and *substance* are used synonymously; but in chemical language the latter word has a more narrow meaning. A **substance** is a species of matter, having constant characters and properties by which it may be recognized, and differentiated from other substance species, irrespective of its shape. Thus sulphur, water, chalk are chemical substances, each of which, in any form in which it may appear, has definite qualities by which it may be distinguished from all other species of substance.

Force is that which produces, or tends to produce motion, or change of motion of matter.

Chemistry.—The simplest definition of chemistry is a modification of that given by Webster: **That branch of science which treats of the composition of substances, their changes in composition, and the laws governing such changes.**

A bar of soft iron may be made to emit light when heated, or sound when caused to vibrate, or magnetism when under the influence of an electric current. Under the influence of these **physical forces** the iron suffers **no change in composition**, and, on cessation of the action of the inciting force the iron returns to its original condition. But if the iron is heated in an atmosphere of oxygen, both the iron and a part of the oxygen disappear, and a new substance, a new chemical species, is produced, having properties of its own, different from those of either the iron or the oxygen. In this case there has been **chemical action**, causing **change of composition**, as the new substance contains both iron and oxygen. The result of such action is, moreover, permanent, and the new product continues to exist, until modified by some new manifestation of chemical action.

While chemical action is thus different in its results from the action of physical forces, there exists the most intimate relation between them. The line of demarcation between chemical actions and certain physical actions, such as solution, although distinct, is narrow. Many chemical actions take place only under certain physi-

cal conditions, such as of temperature; or are provoked by physical forces, such as light.

It is assumed that the student has already acquired a grounding in physics, and that he is in possession of, and uses, a standard text-book on that subject.

GENERAL PROPERTIES OF MATTER.

Indestructibility.—The result of chemical action is change in the composition of the substance acted upon, a change accompanied by corresponding alterations in its properties. Although we may cause matter to assume a variety of different forms, and render it, for the time being, invisible, yet in none of these changes is there the smallest particle of matter destroyed. When carbon is burned in an atmosphere of oxygen, it disappears, and, so far as we can learn by the senses of sight or touch, is lost; but the result of the burning is an invisible gas, whose weight is equal to that of the carbon which has disappeared, plus the weight of the oxygen required to burn it.

Impenetrability.—Although one mass of matter may penetrate another, as when a nail is driven into wood, or when salt is dissolved in water, the ultimate particles of which matter is composed cannot penetrate each other, and, in cases like those above cited, the particles of the softer substance are forced aside, or the particles of one substance occupy spaces between the particles of the other. Such spaces exist between the ultimate particles of even the densest substances.

Divisibility.—All substances are capable of being separated by mechanical means into minute particles. Although we have no direct experimental evidence of a limit to this divisibility, we are warranted in believing that matter is not infinitely divisible. A strong argument in favor of this view is that, after physical subdivision has reached the limit of its power with compound substances, these may be further subdivided into smaller, dissimilar quantities by chemical means. The limit of physical subdivision of matter is the **molecule** of the physicist, the smallest quantity of matter with which he has to deal, the smallest quantity that is capable of free existence (pp. 24, 25).

Inertia—is that negative quality of matter by virtue of which it cannot of itself produce any change in the condition of rest or of motion in which it may be. If matter be at rest it can only be put in motion by the expenditure of work upon it, and, if it be in motion, such motion will continue, rectilinear, uniform, and indefinite, unless interfered with by the interposition of other energy.

Weight.—All bodies attract each other with a force which is in direct proportion to the amount of matter which they contain. The force of this attraction, exerted upon surrounding bodies by the

earth, becomes sensible as weight, when the motion of the attracted body toward the center of gravity of the earth is prevented.

In chemical operations we have to deal with three kinds of weight: **absolute, apparent and specific.**

The Absolute Weight of a body is its weight *in vacuo*. It is determined by placing the entire weighing apparatus under the receiver of an air-pump.

The Apparent Weight, or Relative Weight, of a body is that which we usually determine with our balances, and is, if the volume of the body weighed be greater than that of the counter-poising weights, less than its true weight. Every substance in a liquid or gaseous medium suffers a loss of apparent weight equal to that of the volume of the medium so displaced. For this reason the apparent weight of some substances may be a minus quantity. Thus, if the air contained in a vessel suspended from one arm of a poised balance be replaced by hydrogen, that arm of the balance to which the vessel is attached will rise, indicating a diminution in weight.

Energy is the capacity of matter for doing work. Energy includes both that exertion which is doing work, which is known as **actual or kinetic energy**, and that capacity to do work which is known as **possible or potential energy**. The relative amounts of the two forms change constantly, but their sum is a constant quantity; *i.e., energy, like matter, can neither be created nor destroyed.*

The Specific Weight, or Specific Gravity, or Relative Density of a substance is the weight of a given volume of the substance as compared with the weight of an equal volume of some substance, accepted as a standard of comparison, under like conditions of temperature and pressure. The sp. gr. of solids and liquids are referred to water, and are usually determined at 15°C.; those of gases to air or to hydrogen.

In expressing the sp. gr. of heavy liquids, the weight of one cc. of water is taken as the unit. Thus the sp. gr. of sulphuric acid being 1.84, 1 cc. of water weighing 1 gm., 1 cc. of sulphuric acid weighs 1.84 gms. For light liquids one liter of water is the unit. Thus 1 liter of a liquid of sp. gr. 1026 weighs 1026 gms., or 1.026 kg. In metric, therefore, the weight of 1 cc., or of 1 liter of a liquid represents its specific gravity.

The absolute density of a body is the ratio between its volume and its weight, and is obtained by the formula $D = \frac{P}{V}$, in which D is the density, P the weight, and V the volume. Clearly, also $P = VD$, and $V = \frac{P}{D}$.

When V is taken as the unit of volume the equation $D = \frac{P}{V}$ becomes $D = P$; *i.e., the absolute density of a substance is the weight of*

unit volume of that substance. But as the weight of a given volume of a substance, particularly in the liquid or aëriform state, varies with differences of temperature and of pressure, a definite temperature and pressure have been arbitrarily selected as constituting **normal conditions**. The temperature is 0°C. , and the pressure that of a column of mercury 76 centimeters high at 45° latitude.

Pressures are measured either by the height of a column of mercury which the pressure will sustain in opposition to gravity, in cm. or mm.; or in **atmospheres**, one atm. being the pressure which will sustain a column of mercury of the average height of the barometer; *i. e.*, 760 mm. As the specific gravity (below) of mercury is 13.6 at 0°C. , 1 cc. of mercury weighs 13.6 gms., and each mm. of mercurial column is equivalent to a pressure of 1.36. per sq. cm., and one atm. of pressure is equal to 1033.6 gms. per sq. cm.

The specific volume of a substance (V_s) is the reciprocal of its absolute density: $V_s = \frac{1}{D}$, and is the volume, in cc., which one gram occupies under normal conditions. Thus for hydrogen: $\frac{1}{.00009} = 11111$ cc., or 11.11 L., for oxygen: $\frac{1}{.001429} = 699.7$ cc., and for air: $\frac{1}{.001293} = 773.4$ cc.

States of Matter.—Matter exists in the three forms of solid, liquid and gas (or vapor). The term **fluid** applies to both liquids and gases; the former being distinguished as incompressible, the latter as compressible fluids.

Cohesion is the force by which molecules of the same kind are held together. It is most active in **solids**, which therefore have definite shape and magnitude. In **liquids** it is much less active, yet sufficient to maintain a definite magnitude of the liquid, but it is in part overcome by gravity, which causes the liquid to assume the shape of the containing vessel. In **gases** cohesion is almost nil; therefore, the shape and volume of any gas are those of the containing vessel. Cohesion diminishes with the addition of heat; therefore, by adding heat to a solid it is, if not decomposed, converted into a liquid and then into a gas.

SPECIAL PROPERTIES OF SOLIDS, LIQUIDS AND GASES.

Crystallization.—Solid substances exist in two forms, **amorphous** and **crystalline**. **Amorphous substances** assume no geometric shape; they conduct heat equally well in all directions; they break irregularly; and, if transparent, allow light to pass through them equally well in all directions. A solid in the **crystalline** form has a definite geometrical shape; conducts heat more readily in some directions than in others; when broken, separates in certain directions, called **planes of cleavage**, more readily than in others; and modifies the course of luminous rays passing through it differently when they pass in certain directions than when they pass in others.

Crystals are formed in one of four ways: 1. An amorphous substance, by slow and gradual modification, may assume the crystalline form; as vitreous arsenic trioxide (*q. v.*) passes to the crystalline variety. 2. A fused solid, on cooling, crystallizes; as bismuth. 3. When a solid is sublimed it is usually condensed in the form of crystals. Such is the case with arsenic trioxide. 4. The usual method of obtaining crystals is by the evaporation of a solution of the substance. If the evaporation be slow and the solution at rest, the

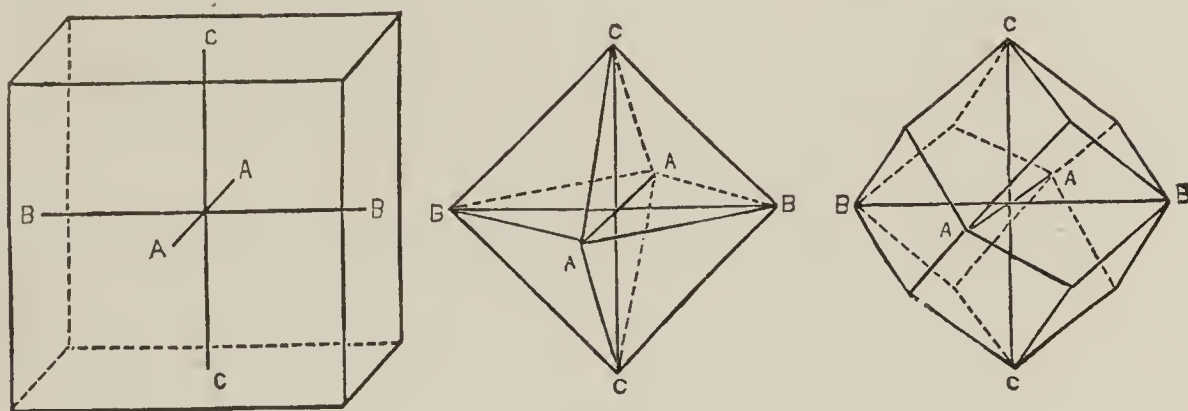


FIG. 1.

crystals are large and well-defined. If the crystals separate by the sudden cooling of a hot solution, especially if it be agitated during the cooling, they are small.

Most crystals may be divided by imaginary planes into equal symmetrical halves. Such planes are called **planes of symmetry**. Thus in the crystals in Fig. 1 the planes *ab ab*, *ac ac*, and *bc bc* are planes of symmetry.

When a plane of symmetry contains two or more equivalent linear

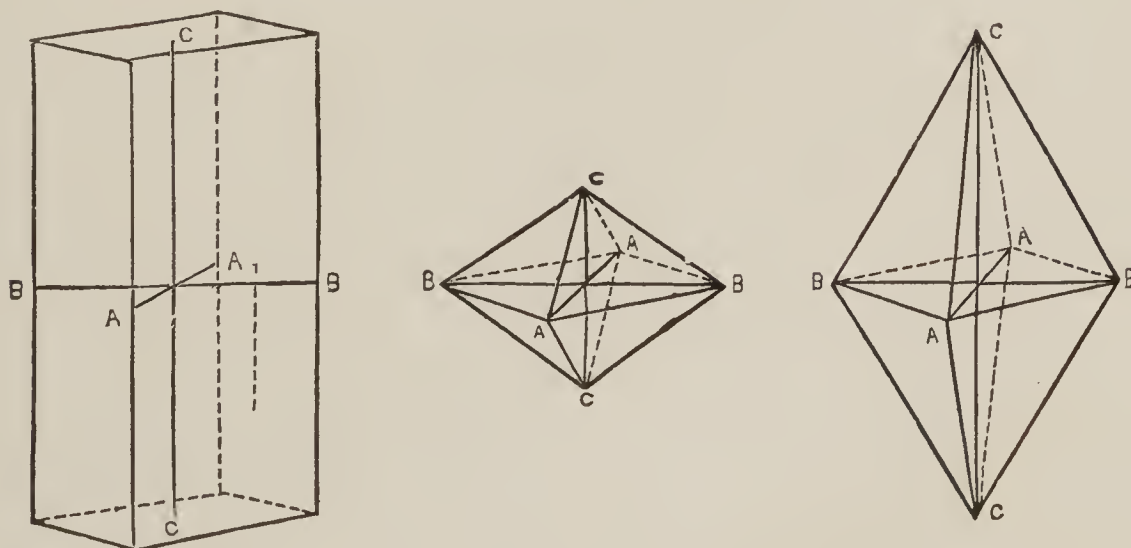


FIG. 2.

directions passing through the center, it is called the **principal plane of symmetry**; as in Fig. 2 the plane *ab ab*, containing the equal linear directions *aa* and *bb*.

Any normal erected upon a plane of symmetry, and prolonged in both directions until it meets opposite parts of the exterior of the

crystal, at equal distances from the plane, is called an **axis of symmetry**.

The axis normal to the principal plane is the **principal axis**. Thus in Fig 2, aa , bb , and cc are axes of symmetry, and cc is the principal axis.

Upon the relations of these imaginary planes and axes a classification of all crystalline forms into six **systems** has been based.

I. The Cubic, Regular, or Monometric System.—The crystals of this system have three equal axes, aa , bb , cc , Fig. 1, crossing each other at right angles. The simple forms are the **cube**; and its derivatives, the **octahedron**, **tetrahedron**, and **rhombic dodecahedron**. The crystals of this system expand equally in all directions when heated, and are not doubly refracting.

II. The Right Square Prismatic, Pyramidal, Quadratic, Tetragonal, or Dimetric System contains those crystals having three axes placed at right angles to each other—two as aa and bb , Fig. 2, being equal to each other and the third, cc , either longer or shorter. The simple forms are the **right square prism** and the **right square based**

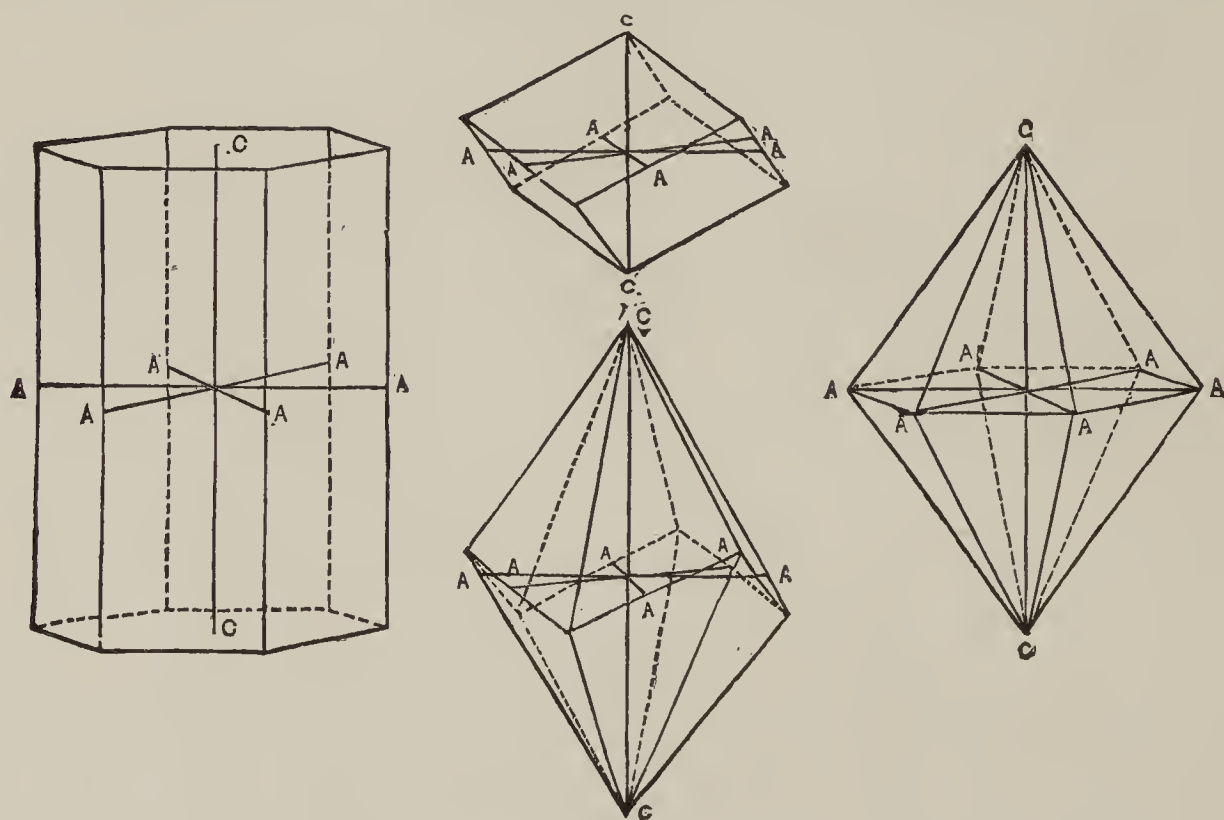


FIG. 3.

octahedron. The crystals of this system expand equally only in two directions when heated. They refract light doubly in all directions, except through one axis of single refraction.

III. The Rhombohedral or Hexagonal System includes crystals having four axes, three of which aa , aa , aa , Fig. 3, are of equal length and cross each other at 60° in the same plane; to which plane the fourth axis, cc , longer or shorter than the others, is at right angles. The simple forms are the **regular six-sided prism**, the **regular dodecahedron**, the **rhombohedral**, and the **scalenohedron**.

These crystals expand equally in two directions when heated, and refract light singly through the principal axis, but in other directions refract it doubly.

IV. **The Rhombic, Right Prismatic, or Trimetric System.**—The axes of crystals of this system are three in number, all at right angles to each other, and all of unequal length. Fig. 2 represents crystals of this system, supposing aa , bb , and cc to be unequal to each other. The simple forms are the **right rhombic octahedron**, the **right rhombic prism**, the **right rectangular octahedron**, and the **right rectangular prism**. The crystals of this system, like those of the two following, have no true principal plane or axis.

V. **The Oblique, Monosymmetric, or Monoclinic System.**—The crystals of this system have three axes, two of which, aa , and cc . Fig. 4, are at right angles; the third, bb , is perpendicular to one and

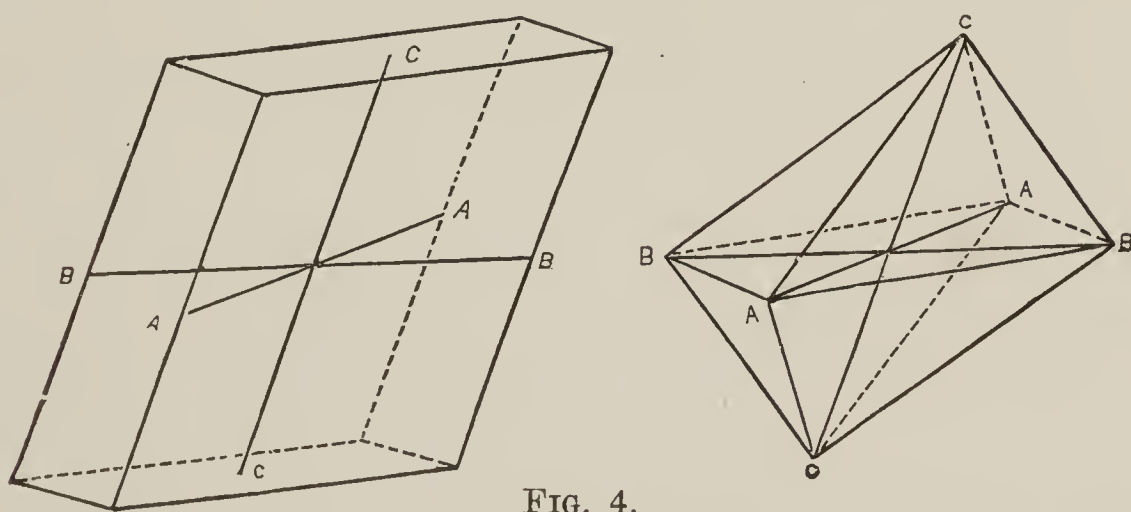


FIG. 4.

oblique to the other. They may be equal or all unequal in length. The simple forms are the **oblique rectangular prism** and **oblique rhombic prism** and **octahedron**.

VI. **The Doubly Oblique, Asymmetric, Triclinic, or Anorthic System** contains crystals having three axes of unequal length, crossing each other at angles not right angles; Fig. 4, aa , bb , and cc being unequal and the angles between them other than 90° .

The crystals of the fourth, fifth, and sixth systems, when heated, expand equally in the directions of their three axes. They refract light doubly except in two axes.

Secondary Forms.—The crystals occurring in nature or produced artificially have some one of the forms mentioned above, or some modification of those forms. These modifications, or **secondary forms**, may be produced by symmetrically removing the angles or edges, or both angles and edges, of the primary forms. Thus, by progressively removing the angles of the cube, the secondary forms shown in Fig. 5 are produced.

It sometimes happens in the formation of a derivative form that alternate faces are excessively developed, producing at length entire

obliteration of the others, as shown in Fig. 6. Such crystals are said to be **hemihedral**. They can be developed only in a system having a principal axis.

Isomorphism.—In many instances two or more substances crystallize in forms identical with each other, and, in most cases, such substances resemble each other in their chemical constitution. They are said to be **isomorphous**. This identity of crystalline form does not depend so much upon the nature of the elements themselves, as

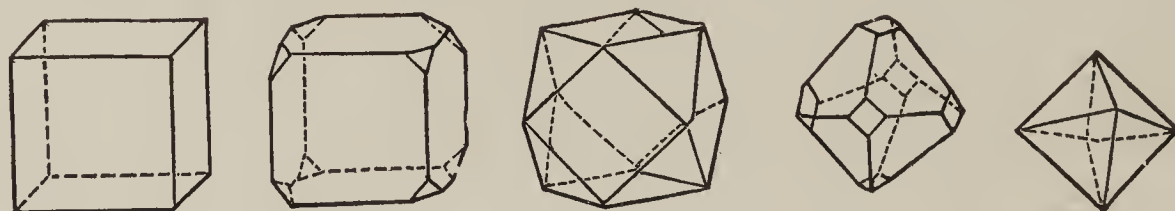


FIG. 5.

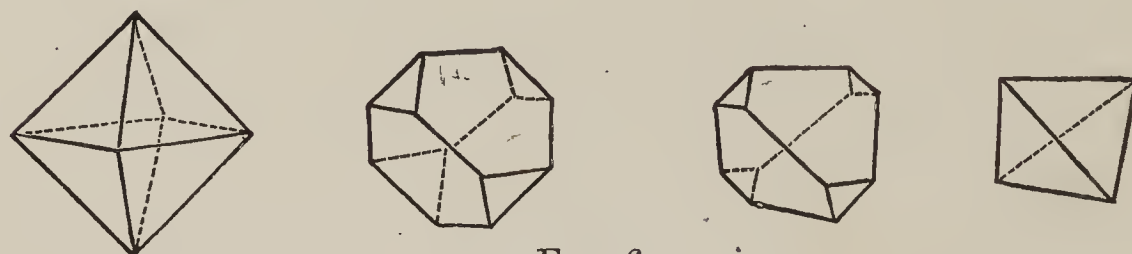


FIG. 6.

upon the structure of the molecule. The protoxide and peroxide of iron do not crystallize in the same form, nor can they be substituted for each other in reactions without radically altering the properties of the resultant compound. On the other hand, all that class of salts known as alums are isomorphous. Not only are their crystals identical in shape, but a crystal of one alum, placed in a saturated solution of another, grows by regular deposition of the second upon its surface. Other alums may be subsequently added to the crystal, a section of which will then exhibit the various salts, layer upon layer.

Dimorphism.—Although most substances crystallize, if at all, in one simple form, or in some of its modifications, a few bodies are capable of assuming two crystalline forms, belonging to different systems. Such are said to be **dimorphous**. Thus, sulphur, as obtained by the evaporation of its solution in carbon disulphide, forms octahedra; when obtained by cooling melted sulphur the crystals are oblique prisms. Occasional instances of **trimorphism**, of the formation of crystals belonging to three different systems by the same substance, are also known.

Many substances on assuming the crystalline form, combine with a certain amount of water which exists in the crystal in a solid combination. Thus nearly half of the weight of crystallized alum is water. This water is called **water of crystallization**, and is necessary to the maintenance of the crystalline form, and frequently to the color. If blue vitriol is heated, it loses its water of crystalliza-

tion, and is converted into an amorphous, white powder. Some crystals lose their water of crystallization on mere exposure to the air. They are then said to **effloresce**. Usually, however, they only lose their water of crystallization when heated (p. 64).

Allotropy.—Dimorphism apart, a few substances are known to exist in more than one solid form. These varieties of the same substance exhibit different physical properties, while their chemical qualities are the same in kind, but differ in their degrees of activity. Such modifications are said to be **allotropic**. One or more allotropic modifications of a substance are usually crystalline, the other or others amorphous or vitreous. Sulphur, for example, exists not only in two dimorphous varieties of crystals, but also in a third, allotropic form, in which it is flexible and amorphous. Carbon exists in three allotropic forms: two crystalline, the diamond and graphite; the third amorphous. For other examples of allotropy, see ozone, phosphorus, and silicon.

In passing from one allotropic modification to another, a substance absorbs or gives out heat.

Diffusion of Liquids—Dialysis.—If a liquid is carefully floated upon the surface of a heavier liquid, with which it is capable of mixing, two distinct layers are at first formed. But, even at perfect rest, mixing of the two liquids, in opposition to gravity, will begin immediately, and progress slowly until the two liquids have **diffused** into each other to form a single liquid whose composition and density are the same throughout.

If, in place of bringing the two liquids into direct contact, they are separated from each other by a membrane of goldbeater's skin, each will pass through the membrane into the other, a phenomenon called **osmosis**, but they do not pass with equal rapidity. Thus, if the two liquids are alcohol and water, one part of alcohol will pass in one direction while 4.2 parts of water pass in the other. This relation, as compared with water, is the **osmotic equivalent** of the substance, and may be determined not only for liquids, but also for solids in solution.

If a layer of a pure solvent (p. 14) is similarly floated upon a solution of a solid in the same liquid, as water upon a solution of sugar, or if the two are separated by a membrane of parchment paper, bladder, or other **permeable membrane**, the pure solvent will pass into the solution, and the dissolved sugar into the pure solvent until the two liquids have the same **concentration**, *i. e.*, contain the same quantity of dissolved substance in unit volume throughout. (See solution, p. 14.)

Solids in solution differ in the rapidity and completeness with which they undergo osmosis, or dialyse. Substances which crystallize, **crystalloids**, dialyse easily and with relative rapidity; those which do not form crystals, **colloids**, do not dialyse, or do so with extreme

slowness. Advantage is taken of this difference to separate crystalloids from colloids, as salt from albumin. The solution of the two substances is placed in the inner vessel of a **dialyser** (Fig. 7), whose bottom consists of a layer of parchment paper, and the outer vessel is filled with the pure solvent, water, which is frequently changed as the crystalloid collects in it. Or a section of tubing made of parchment paper, bent into a U shape, may be used as the inner vessel, and suspended in water. Plates of porous earthenware may also be used for dialysis of liquids which would attack an animal

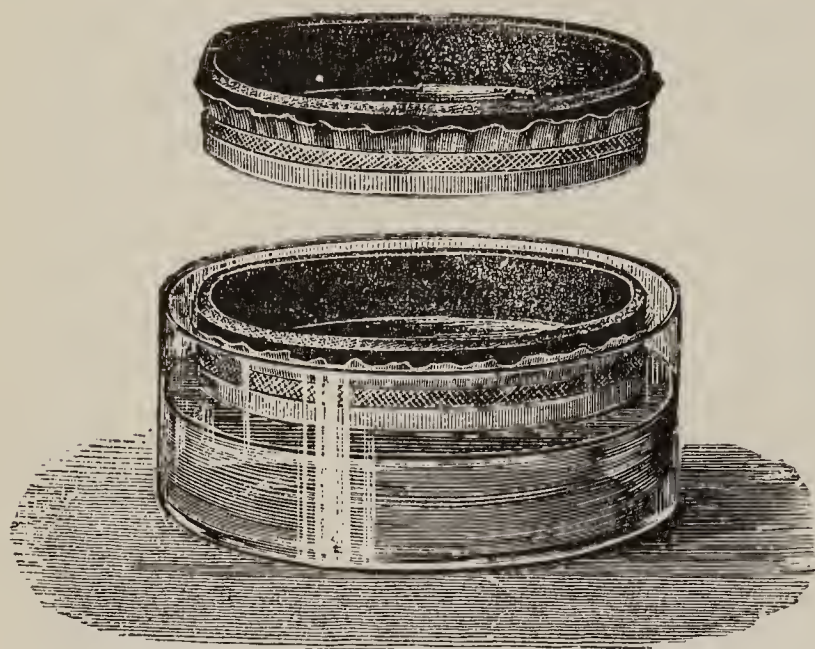


FIG. 7.

or vegetable membrane, but their action is much slower. **Semipermeable membranes** are membranes which are permeable to certain diffusible substances, but not to others, usually permeable to water but not to certain substances in solution in it. Such membranes exist in animal and vegetable nature and are formed artificially. Pfeffer's membrane is obtained by placing a solution of cupric sulphate in a jar of porous earthenware, which is then

immersed in a solution of potassium ferrocyanide. A delicate, gelatinous film of cupric ferrocyanide forms in the walls of the jar where the two solutions come in contact, which constitutes the semipermeable membrane, permeable to water and to saltpeter dissolved in water, but not to sugar or to many other substances in aqueous solution. (See Osmosis, p. 9.)

Gases when subjected to pressure diminish in volume progressively to an amount limited only by their passage to the form of liquid (p. 15). When relieved of pressure they expand to an unlimited extent. They have, therefore, the volume of the containing vessels, upon whose walls they exert a pressure corresponding to that to which they are themselves subjected, and in all parts of which they have the same density.

Boyle-Mariotte Law.—If any gas, maintained at a constant temperature, is contained in a vessel whose capacity may be altered, as by a piston, the pressure exerted by the gas is found to be doubled when the capacity of the vessel is reduced to one-half; and corresponding variations of pressure are observed with other changes in volume:

The temperature remaining the same, the volume of a given quantity of gas is inversely as the pressure (Boyle-Mariotte Law). Or:

$vp=\text{constant}$. It also follows that *the density of a gas is proportionate to the pressure*.

Absorption of Gases.—Physical solution (p. 14) of a gas in a liquid is called **absorption**. The absorption of gases by liquids obeys the following laws:

The weight of a gas absorbed by unit volume of a given liquid is proportionate to the gas pressure (Henry's law).

The quantity of gas absorbed diminishes with increase of temperature.

The quantity of a gas which a liquid can absorb is independent of the nature and quantity of other gases which it may already hold in solution.

Some solid substances also absorb certain gases. Sometimes such absorption is a physical act, when it is referred to as **condensation** or **absorption**. Thus charcoal condenses about 90 times its volume of ammonia. In other cases it is a chemical combination, as when caustic potash absorbs carbon dioxide.

SOME PHYSICAL ACTIONS OF CHEMICAL INTEREST.

HEAT.

The **Effects of Heat** upon a body are in doing *internal work*: to raise its temperature, to increase its volume, to change its state of aggregation, or to cause atomic rearrangement, *i. e.*, chemical change, or in doing *external work*: in exerting pressure, or in transmitting heat to surrounding bodies.

Temperature.—The temperature of a body is the extent to which it can impart sensible heat to surrounding bodies. It is not to be confounded with the *amount* or *quantity of heat* which the body contains. A block of ice just beginning to melt and the same weight of water just beginning to freeze have the same temperature; but heat must be added to the ice to continue its fusion and subtracted from the water to continue its solidification, while during both processes the temperature remains the same in each.

Thermometers are instruments for the measurement of temperature. They are usually glass tubes having a bulb blown at one end and closed at the other, the bulb and part of the tube being filled with mercury or with alcohol, whose contraction or expansion indicates a fall or rise of temperature. The alcoholic thermometer is used for measuring low temperatures, and the mercurial for temperatures between -40° and 360° C. For higher temperatures instruments called **pyrometers**, based upon the expansion or variation of electrical conductance of solids, are used.

In every thermometer there are two *fixed points*, determined by experiment. The lower, or **freezing point**, is fixed by immersing the instrument in melting ice, and marking the level of the mercury in the tube upon the glass when it has become stationary. The higher,

or **boiling point**, is similarly fixed by suspending the instrument in the steam from boiling water. The instrument is then graduated according to one of three **scales**: the **Celsius**, or **Centigrade**, the **Fahrenheit**, and the **Réaumur**. The freezing point is marked 0° in the Centigrade and Réaumur scales, and 32° in the Fahrenheit. The boiling point is marked 100° in the Centigrade, 212° in the Fahrenheit, and 80° in the Réaumur scale (Fig. 8).

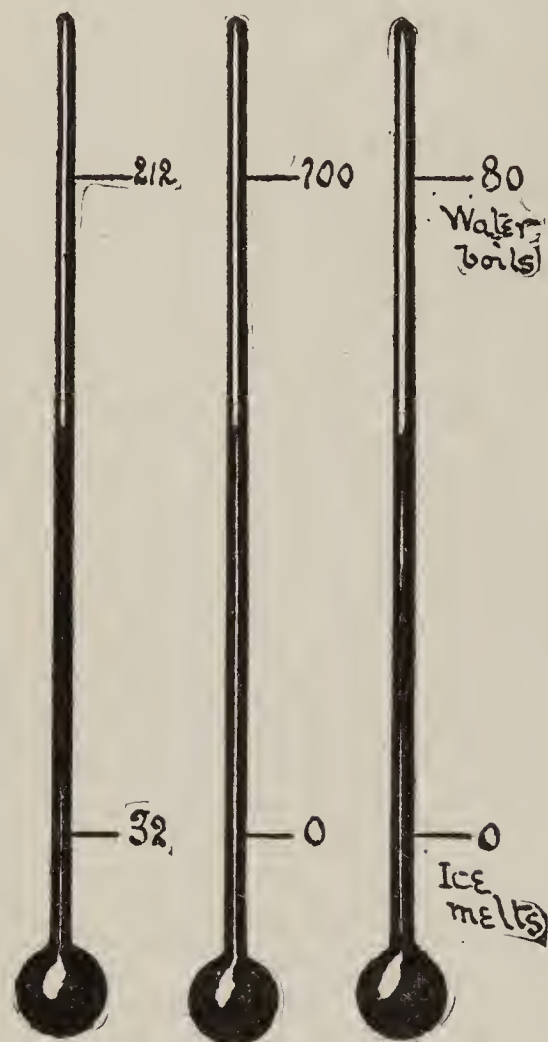


FIG. 8.

The space between the fixed points is divided into 100 equal **degrees** in the Centigrade scale, into 180° in the Fahrenheit, and into 80° in the Réaumur. Five degrees Centigrade are therefore equal to nine degrees Fahrenheit.

To convert readings in one scale into terms of another the following formulæ are used:

Centigrade to Fahrenheit: Multiply by 9, divide by 5, and add 32. Example: $50^{\circ}\text{C.} \times 9 = 450 \div 5 = 90 + 32 = 122^{\circ} = \text{Ans.}$

Fahrenheit to Centigrade: Subtract 32, multiply by 5, and divide by 9. Example: $5^{\circ}\text{F.} - 32 = -27 \times 5 = -135 \div 9 = -15^{\circ} = \text{Ans.}$

The Centigrade scale is the one now exclusively used for scientific work, and is the only one referred to throughout this volume.

Measure of Heat.—Heat is measured by its effect in raising the temperature of a given weight of water through a given number of degrees of temperature. Several units have been used, and, unless definitely stated, may easily lead to confusion.

The **calorie**, or **therm**, or **small calorie**, or **gram-calorie** (cal.) is the amount of heat required to raise the temperature of one gram of water from 0° to 1°C. (or from 4° to 5°C.). The **rational calorie** (K) is the amount of heat required to raise the temperature of one gm. of water from 0° to 100°C. , and is nearly equal to 100 cal. The **large calorie**, or **kilogram calorie** (kg:cal.), is based upon the raise of temperature of one kilogram of water from 4° to 5°C. , and is equal to 1000 cal.

Changes in Volume Caused by Heat.—As a rule, all substances increase in volume when heated, and diminish in volume on losing heat. There are, however, some exceptions to this rule.

Solids and liquids change only slightly in volume by heating or

cooling. Thus the **coefficient of linear expansion**, or ratio of variation in length, of steel is .0000124, and the **coefficient of cubic expansion**, of variation in volume of mercury is .00018 for 1°C . Water on being cooled contracts until its temperature is 4°C ., between which and 0° it again expands; 4°C . is, therefore, the **temperature of maximum density of water**.

The changes in volume of *gases* by heat are of much greater theoretical importance than those in solids and liquids.

We have seen that the volume of gas varies with the pressure in obedience to the law: $VP = \text{constant}$. This is only true if the temperature remain constant. With variation in temperature the volume of a gas varies according to

The Dalton--Gay-Lussac Law:—*The pressure remaining constant, the volume of a gas varies directly with the absolute temperature* (see below). And, conversely, *if the volume remain constant, the pressure varies directly with the temperature*.

The Law of Charles is to the effect that *all gases have the same coefficient of expansion*.

Absolute Zero—Absolute Temperature.—As gases contract by $\frac{1}{273}$ of their volume with each degree of diminution of temperature, a unit volume of gas at 0° on continuous cooling would occupy zero volume at -273° . As it is assumed that at that temperature a gas contains no heat -273° is taken as the **absolute zero**, and degrees of **absolute temperature** are from that point: $T = 273 + t$. Thus, if the observed temperature, t , be 54°C . the absolute temperature, T , is $273 + 54 = 327$. No gas is known to exist at so low a temperature as -273° ; the most resistant, hydrogen, forms a liquid which boils at -252.5° , and this temperature can only be slightly lowered by reducing the pressure. The lowest temperature yet attained is -263° .

Change of State.—The state of aggregation of matter depends partly upon the pressure to which it is subjected, but principally upon the amount of heat which it contains. If chemical decomposition does not occur, when heat is added to a solid the motion of its molecules becomes more rapid, and their cohesion becomes less, until the solid becomes a liquid. With the addition of more heat the molecules are more widely separated, their cohesion is reduced to the minimum, and the liquid becomes a vapor. The reverse order of change is produced by abstraction of heat, popularly referred to as “cooling.”

Solids assume the liquid form by *fusion* or by *solution*.

Fusion.—When a solid, not decomposed by heat, is sufficiently heated it **fuses**, or **melts**. Substances which withstand a high temperature without fusion are said to be **refractory**. Every substance begins to fuse at a certain temperature, which is always the same for a given substance, the pressure remaining constant, and which

remains the same until fusion is complete, whatever the intensity of the heat applied. This temperature is called the **fusing point** of the substance, and is one of the characters depended upon for its identification, and as a test of its purity. Some substances pass by imperceptible changes of gradual softening from the condition of solid to that of liquid, the temperature rising the while, and therefore have no true fusing point; such are iron and glass.

The fusing point is only slightly influenced by the pressure. That of substances which contract on fusion is slightly lowered by increase of pressure, and that of those which expand on fusion is slightly raised.

Latent heat.—As during the fusion of a solid there is no increase of temperature, notwithstanding that heat is being constantly communicated to the body, the insensible heat so added, which really does work, is said to become **latent**. Each substance has its own latent heat, or **latent heat of fusion**, as it is also called. Thus, if a pound of water at 0°C . is placed in one vessel, and in another similar vessel a pound of ice at 0°C ., and the two vessels then immersed in a large vessel of hot water until the ice is melted, the temperature of the melted ice will be found to be 0°C ., while the temperature of the water, previously at 0° will be found to be 79.25°C .; therefore the amount of heat which became latent in melting the ice was 79.25° .

Solution.—A solid, liquid or gas is said to **dissolve**, or to form a **solution** in a liquid, when the two substances form a homogeneous liquid. The molecules of the dissolved substance, the **solute**, are assumed to be uniformly distributed among the molecules of the liquid, which is called the **solvent**.

The act of solution may be a purely physical process, without chemical action between the solute and the solvent, in which case it is referred to as **physical** or **simple solution**; or it may consist of two distinct acts, one a chemical action between solute and solvent, and the other the physical solution of the new substance thus produced, in which case it is called **chemical solution**. A physical solution contains the original substance, which, if a solid, can be recovered unchanged by evaporation of the solution, as cupric nitrate from a solution of that salt, however obtained. A chemical solution is, in fact, a physical solution of the new substance formed in the reaction, as cupric nitrate is also left on evaporation of a solution of copper in nitric acid.

The quantity of a single solid which can be dissolved in a pure solvent, water for instance, depends upon an inherent relation between solvent and solute, called the **solubility**, and upon the temperature. The solubility of a solid is one of its distinguishing characters, and each solid has a definite solubility in a given liquid at a given temperature. When no solvent is mentioned, water is understood.

Some solids, such as calcium chloride, are so readily soluble in water that they absorb sufficient from the air to form a solution. They are then said to **deliquesce**.

The solubility of most solids increases with rise of temperature. With some the increase of solubility is proportionate to the rise of temperature, with others the solubility is very slightly affected by variation of temperature, and with others there is a certain temperature of maximum solubility, above which it again diminishes.

A solution containing as much of the solute as it is capable of dissolving at the existing temperature is said to be **saturated**. If made at high temperature it is said to be a **hot saturated**, and if at the ordinary temperature a **cold saturated solution**. If a hot saturated solution, or one containing more solid than the liquid is capable of dissolving at a lower temperature, be cooled, the solid usually separates in the crystalline form. But if, in the case of certain substances, the solution is allowed to cool while undisturbed, no crystallization occurs, and the solution at the lower temperature contains a larger amount of the solid than it could dissolve at that temperature. It is then said to be **supersaturated**. If a given quantity of liquid be brought in contact with a quantity of solid less than it can dissolve at the existing temperature, the solid dissolves completely to form an **unsaturated solution**; while if it be in contact with any excess of the solid, such excess remains undissolved, and has no influence upon the solution so long as the temperature remains constant. The solubility of solids is also influenced by the pressure, but to so trifling an extent that it may be disregarded. **Dilute solutions** are such as contain very small quantities of the solutes.

Congelation is the passage of a substance from the liquid to the solid form. It is the reverse of fusion, and takes place at the same fixed temperature, which also remains constant until fusion is complete. This temperature is called the **freezing point** of the substance.

Vaporization.—The passage of a liquid to an aëriform state may take place from the surface of the liquid only, when the process is called **evaporation**, or it may take place throughout the mass of the liquid, when it is called **ebullition**, or **boiling**. Liquids which evaporate readily, as alcohol, chloroform, ether, are distinguished as **volatile liquids**; while liquids which do not evaporate, like the fixed oils and glycerol, are called **fixed liquids**.

Gases and Vapors.—All aëriform bodies have been converted into liquids under the combined influence of cold and pressure.

Aëriform bodies exist in two conditions, dependent upon the temperature. For each gas there is a certain temperature, different for different gases, at and below which the gas can be converted into a liquid by sufficient increase of pressure, without further lowering of temperature, but above which no amount of pressure will cause liquefaction. That temperature is called the **critical temperature**.

At temperatures above their critical temperatures aëriiform bodies are **gases**, below that temperature they are **vapors**. When the substance is at its critical temperature there is a certain definite pressure which will cause its liquefaction, which is called its **critical pressure**. For example: the critical temperature of carbon dioxide is 31.1° , and its critical pressure 75.56 atm.

When a liquid is heated in a sealed glass tube of sufficient strength to withstand the high pressure attained, a temperature is finally reached when the liquid disappears, and the tube is filled with its vapor, which, having the same volume and weight as the liquid, also has the same density. The temperature at which this occurs, 190° for ether, is clearly the critical temperature of the substance, which is therefore also called its **absolute boiling point**, and the pressure in the tube is its critical pressure. There is also necessarily a **critical density**, *i. e.*, the weight of unit volume of the substance at its critical temperature and pressure.

Boiling.—At a given pressure a liquid begins to boil at a certain temperature, which varies in different liquids, but is always the same in the same liquid. This temperature at 760 mm. of pressure is the **boiling point** of the liquid.

The boiling point remains stationary until the liquid is completely volatilized, whatever the degree of the heat applied.

The boiling point is raised by increase of pressure, and depressed by diminution of pressure.

Latent heat of vapor.—The heat required by a liquid to convert it into a vapor, which is insensible as temperature, is the **latent heat of vapor** (p. 14).

A liquid, in evaporating, absorbs heat. It is by this action that the human body is cooled by the evaporation of perspiration from the skin, that local anesthesia is produced by the evaporation of very volatile liquids, and that cold is produced in refrigerating machines.

Liquefaction or condensation is the passage of a gas or vapor to the form of a liquid. It is brought about by chemical action, by cooling, and by compression.

Certain salts, such as calcium chloride, absorb vapor of water from the air and with it form a solution. They are then said to **deliquesce**.

When vapors are cooled to a temperature below the boiling point of the liquid from which they originated, at the existing pressure, they are condensed.

The process of **distillation** consists in converting a liquid into a vapor by heat and subsequently condensing the vapor by cooling it. Distillation under reduced pressure is frequently resorted to when it is desirable to avoid a temperature as high as the boiling point of the liquid. **Fractional distillation** is the separation of liquids of

different boiling points by distillation and collection of the several fractions separately.

Sublimation is a process differing from distillation in that the material acted upon and the product are solid. Sublimation may or may not be attended by fusion of the original substance. The product is called a **sublimate**, or, if in fine powder, **flowers**.

Specific Heat.—Equal weights of different substances do not possess the same capacity for heat or **thermal capacity**. Thus if equal weights of water and of mercury are exposed to the same source of heat until the water shall have acquired a temperature of 1° C., the mercury will have a temperature of 30° . A given weight of water, therefore, requires 30 times as much heat to raise its temperature through 1° as does an equal weight of mercury, and the capacity for heat of mercury is $\frac{1}{30}$, or 0.0333, that of an equal weight of water.

The **specific heat of a substance** is the amount of heat required to raise the temperature of one kilo. of that substance through one degree Centigrade, expressed in calories. Thus, the specific heat of mercury is 0.0333, as stated above.

ELECTRICITY.

Certain substances, such as amber, glass, sealing-wax, when rubbed with silk, flannel, etc., acquire the power of attracting light bodies. They are then said to be **electrified**.

If a glass rod is rubbed with silk and approached to a pith ball suspended by a silk thread from a glass support, the pith ball is first attracted, and, after a short contact with the glass, is then repelled. The pith ball has become electrified by contact with the glass, and in this condition the two bodies repel each other. But if now a rod of sealing-wax is rubbed with flannel and approached to the electrified pith ball, the rod will attract the ball. In this state the ball is repelled by the electrified glass, and attracted by the electrified sealing-wax. And, similarly, a pith ball electrified by contact with the electrified sealing-wax will be repelled by the wax and attracted by the glass rod. There are, therefore, two kinds of electricity, one generated in glass by friction with silk, called **vitreous** or **positive** (+) electricity, the other generated in sealing-wax by friction with flannel, called **resinous**, or **negative** (—) electricity.

Bodies similarly electrified repel each other, and bodies differently electrified attract each other.

Insulators—Conductors—Ions.—If two metal spheres, supported upon glass rods, and placed about a foot apart, are charged, one with positive, and the other with negative electricity, the spheres will attract each other, but each will retain its charge in dry air. If, now, a glass rod is brought in contact with both spheres at the same time, each still retains its charge as before. But if a brass rod is used in

place of the glass one, the positive and negative electricities neutralize each other, and both spheres lose their charges. Glass is an **insulator**, or **non-conductor** of electricity; brass is a **conductor**. Conductors are of two kinds: **Conductors of the first order**, such as metals, conduct electricity without themselves suffering any change, except elevation of temperature. **Conductors of the second order**, such as solutions of salts, are substances from which their constituents are separated by the passage of electricity through them. The constituents which are thus separated from a conductor of the second order are called **ions** (pp. 20, 35). Another distinction between the two orders of conductors is that with those of the first order electrical energy only is transported, while with those of the second order matter (the ions) is also transported.

Galvanic Electricity.—The kinetic energy which is developed in chemical solution of a metal is manifested in part as heat, but also

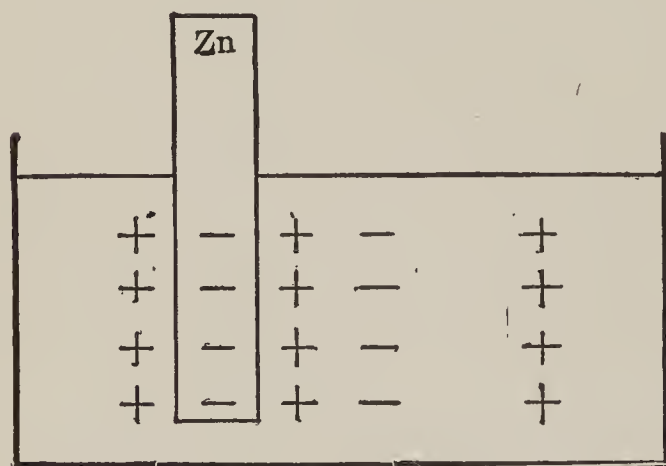


FIG. 9.

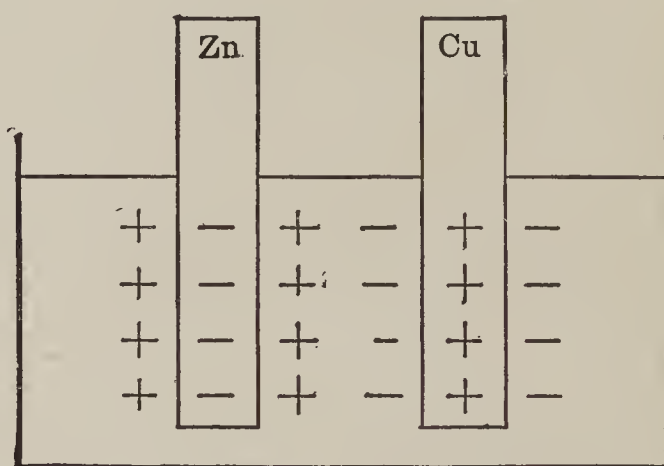


FIG. 10.

in great part in charging the metal with negative electricity, and the solvent with positive electricity. Thus, if a plate of pure zinc is immersed in pure dilute sulphuric acid, the metal becomes charged with negative electricity, and at the same time a part of the zinc goes into solution, its ions carrying a positive charge to the surrounding liquid (Fig. 9). This action continues for a very short time, until the electric charge so produced balances the "solution pressure" of the metal, *i. e.*, its tendency to dissolve when all action ceases. If, now, a plate of pure copper is also immersed in the acid, the solution pressure of this metal being extremely small, the copper simply becomes charged with positive electricity, and the surrounding liquid with negative electricity; but no further solution of the zinc occurs (Fig. 10). If, now, the two metal plates are connected by a conducting wire, the negative electricity of the zinc and the positive of the copper neutralize each other along the conductor (Fig. 11), the electric charges of the liquid recombine, and solution of the zinc again begins, attended by the generation of constantly renewed electric charges, which constantly tend to neutralize each

other, producing an **electric current**, which consists of the passage of positive electricity in one direction, and of negative electricity in the opposite direction.

An arrangement of metals and solvent such as that described is called a **galvanic cell** or **element**, and a combination of two or more is a **galvanic battery**.

An electric current is produced whenever two metals, or a metal and another conducting solid, are immersed in a liquid in which the two solids have different solution pressures, or when two plates of the same kind of metal are immersed in two liquids in which the metal has different solution pressures, and either floated one upon the other, or separated only by a porous diaphragm. The metal having the higher solution pressure is the one which is dissolved in the action of the galvanic element, and hence is the position of higher potential. The other plate is the position of lower potential. Any wires or other conductors attached to the plates are called **poles**, or **leads**, or **electrodes**. The entire system of solvent, plates and outside conductors is called an **electric** or **galvanic circuit**. The

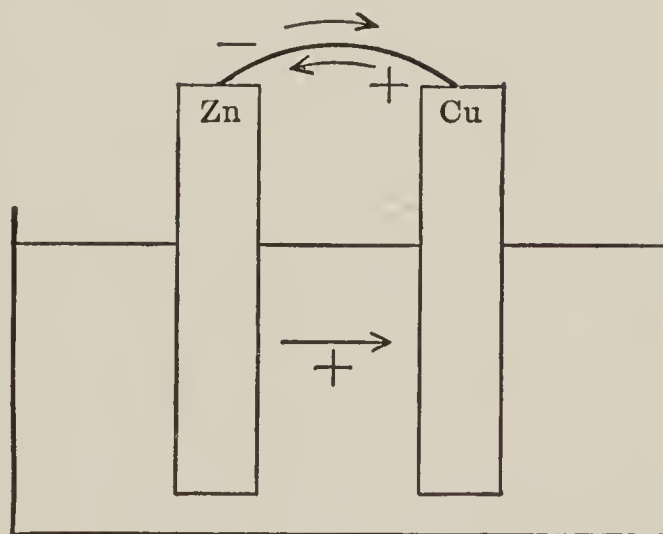


FIG. 11.

circuit is said to be **closed** when there is no break in its continuity, and the current is free to pass. It is said to be **open** when there is an interruption in its continuity, when the current ceases to pass.

The positive electrical current originates at that plate having the greater solution pressure, *i. e.*, the higher potential (the zinc plate, Fig. 11), which is therefore called the **generating**, or **positive plate**. It flows through the liquid in the cell to the plate of lower potential (the copper plate), which is therefore called the **collecting**, or **negative plate**. From the collecting plate the current passes through the outside conductors of the circuit toward the generating plate. As the positive current leaves the cell from the negative plate, the electrode connected with that plate is of higher potential than that connected with the generating plate, and therefore we have the apparent anomaly that the pole connected with the negative plate is called the **positive pole**, or the **anode**, while the pole connected with the positive plate is called the **negative pole**, or the **cathode**, or **kathode**. The positive current, therefore, passing from the position of higher potential to that of lower potential, in many respects resembles the flow of water from a higher to a lower level, or the passage of heat from a higher to a lower temperature. The negative current, on the other hand, passes from lower to higher potential.

The total current is the sum of the passage of positive charges in one direction and of negative charges in the opposite direction.

Electromotive Force—Resistance.—The difference in potential of an electric generator is referred to as its **electromotive force** (E. M. F.).

The strength of the current is directly as the E. M. F., and inversely as the resistance, and, consequently, the current strength is the E. M. F. divided by the resistance (Ohm's law).

We have seen that some substances conduct electricity, while others do not. Conductors also differ in the degree of facility with which they allow the current to pass through them when they are of equal length and of equal cross-section. The **resistance** of a conductor is the degree of opposition which it offers to the passage of the current, and the complement of the resistance is the **conductance** of the conductor. Resistance and conductance are clearly inversely proportionate to each other. They depend upon four factors: 1. The special property of conductivity of the material; 2. The length of the conductor; 3. Its cross-section; 4. The temperature. The resistance is directly as the length, and inversely as the cross-section of the conductor. With metals it is increased, and with salt solutions it is diminished by elevation of temperature. In considering the resistance of a galvanic circuit we have to deal with both **internal resistance**, *i. e.*, that of the liquid, or liquids, and plates composing the elements, and **external resistance**, *i. e.*, that of the conducting system outside of the battery.

Ohm's Law.—This fundamental empirical law is to the effect that: *The current strength is directly proportionate to the electromotive force, and inversely proportionate to the resistance.* Or: $C = \frac{E}{R}$, and consequently: $R = \frac{E}{C}$, and $E = RC$, also.

Electrolysis.—We have seen (p. 18) that when a current passes through a conductor of the second order certain constituents, called ions, are separated from the conductor. This occurs with all liquids, whether solutions or fused solids, which are conductors, and the process is called **electrolysis**, while the substance acted upon, the conductor, is called an **electrolyte**. The ions are given off, one at each electrode, and entirely unmixed with each other. Those that are given off at the positive electrode, or anode, being attracted thereby, are charged with negative electricity, and are therefore **electronegative ions**, or **anions**. Those which are given off at the negative electrode, or cathode, are **electropositive ions**, or **cations**. Thus, when water is electrolyzed, pure hydrogen is given off at the negative electrode, and pure oxygen at the positive electrode; and when hydrochloric acid solution is electrolyzed pure hydrogen is again given off at the negative electrode, and pure chlorine gas at the positive. (See p. 33.)

Electrical Units.—The **Ohm** is the unit of resistance. It is the resistance offered by a column of mercury, at 0° C., 106.3 cent. long, weighing 14.4521 gm., and having a uniform cross-section of 1 sq. mm. The **Megohm**, for the measurement of high resistances, is 1,000,000 ohms; and the **Microhm**, for the measurement of small resistances, is $\frac{1}{1,000,000}$ ohm.

The **Ampère** is the unit of current strength. It is a current which will deposit 4.025 gm. of metallic silver in one hour from a neutral solution of silver nitrate (see electrolysis). A **milliampère** is $\frac{1}{1000}$ ampère.

The **Volt** is the unit of E. M. F. It is that E. M. F. which, acting steadily through a conductor having a resistance of one ohm will produce a current of one ampère. It is also $\frac{1000}{1438}$ the E. M. F. of a standard Clark's cell at 15° C.

The **Coulomb** is the unit of electrical quantity. It is the quantity of electricity transferred in one second by a current of one ampère.

The **Farad** is the unit of capacity. It is the capacity of a condenser charged to a potential of one volt by one coulomb of electricity.

The **Watt** is the unit of energy. It represents the work done by one ampère with a pressure of one volt. One watt per second is equal to $\frac{1}{746}$ of a horse power, or 44.236 foot pounds. The kilowatt, 1000 watts, is the unit used by electrical engineers.

CHEMICAL PHENOMENA.

Elements.—Most substances may be so decomposed as to yield two or more other substances, distinct in their properties from the substance from whose decomposition they resulted, and from each other. If, for example, sugar is treated with sulphuric acid, it blackens, and a mass of charcoal separates. Upon further examination we find that water has also been produced. From this water we may obtain two gases, differing from each other widely in their properties. Sugar is therefore made up of carbon and the two gases, hydrogen and oxygen; but it has the properties of sugar, and not those of either of its constituent parts. There is no method known by which carbon, hydrogen and oxygen can be split up, as sugar is, into other dissimilar substances.

An **element** is a substance which cannot by any known means be split up into other dissimilar bodies.

Elements are also called **elementary substances** or **simple substances**.

The number of well-characterized elements at present known is eighty-three (list p. 27, see also p. 54). Of these eighty-three elements comparatively few enter into the composition of the earth's

crust (with the atmosphere and water), and about ten of them constitute approximately 97 or 98 per cent. of the whole. These, with the approximate proportions of each, are:

Oxygen 50 per cent.	Sodium 2.5 per cent.
Silicon 25 “ “	Potassium 2.5 “ “
Aluminium 7 “ “	Magnesium 2 “ “
Iron 4 “ “	Hydrogen 1 “ “
Calcium 3 “ “	Titanium 0.5 “ “
	<hr/>
	Total 97.5 “ “

It will be noticed that elements which are of great importance in their relation to life (such as carbon, nitrogen, phosphorus, sulphur, and chlorine) and such valuable and useful elements as gold, silver, and mercury,—all combined only furnish about 2.5 per cent. of the total.

The elements found in the human body are carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, fluorine, chlorine, iodine, silicon, sodium, potassium, calcium, magnesium, lithium, iron, and occasionally traces of manganese, copper, and lead.

Compounds are substances made up of two or more elements chemically united with each other in definite proportions. Compounds exhibit properties of their own which differ from those of the constituent elements to such a degree that the properties of a compound can never be deduced from a knowledge of those of the constituent elements. Common salt, for instance, is composed of 39.4 per cent. of the light bluish-white metal, sodium, and 60.6 per cent. of the greenish-yellow, suffocating gas, chlorine.

Compounds made up of two elements only are called **binary** compounds; those consisting of three elements, **ternary** compounds; those containing four elements, **quaternary** compounds, etc.

A **mixture** is composed of two or more substances, elements or compounds, mingled in any proportion, without chemical action between the constituents. The characters of a mixture may be predicated from a knowledge of the properties of its constituents. Thus sugar and water may be mixed in any proportion, and the mixture will have the sweetness of the sugar, and will be liquid or solid, according as the liquid or solid ingredient predominates in quantity.

Laws governing the combination of elements.—THE LAW OF DEFINITE PROPORTIONS.—The relative weights of elementary substances in a compound are definite and invariable. If, for example, we analyze water, we find that it is composed of eight parts by weight of oxygen for each part by weight of hydrogen, and that this proportion exists in every instance, whatever the source of the

water. If, instead of decomposing, or **analyzing** water, we start from its elements, and by **synthesis** cause them to unite to form water, we find that, if the mixture be made in the proportion of eight oxygen to one hydrogen by weight, the entire quantity of each gas will be consumed in the formation of water. But if an excess of either have been added to the mixture, that excess will remain after the combination.

THE LAW OF MULTIPLE PROPORTIONS.—When two elements unite with each other to form more than one compound, the resulting compounds contain simple multiple proportions of one element as compared with a constant quantity of the other.

Oxygen and nitrogen, for example, unite with each other to form five compounds. In these the two elements bear to each other the following relations by weight:

In the first, 14 parts of nitrogen to $8 \times 1 = 8$ of oxygen.
In the second, 14 parts of nitrogen to $8 \times 2 = 16$ of oxygen.
In the third, 14 parts of nitrogen to $8 \times 3 = 24$ of oxygen.
In the fourth, 14 parts of nitrogen to $8 \times 4 = 32$ of oxygen.
In the fifth, 14 parts of nitrogen to $8 \times 5 = 40$ of oxygen.

THE LAW OF RECIPROCAL PROPORTIONS.—The ponderable quantities in which substances unite with the same substance express the relation, or a simple multiple thereof, in which they unite with each other. For example: 71 parts of chlorine combine with 40 parts of calcium, and 16 parts of oxygen also combine with 40 parts of calcium, therefore 71 parts of chlorine combine with 16 parts of oxygen, or the two elements combine in the proportion of some simple multiples of 71 and 16.

Mixtures of solids are usually mechanical mixtures, but in some instances the particles of solid mixtures are so intimately intermingled that the products are referred to as **solid solutions**. Indeed, when one constituent predominates largely, there is reason to believe that “dissociation” may occur, as in dilute liquid solutions. **Isomorphous mixtures** are crystals obtained by evaporation of mixed solutions of isomorphous compounds, such as the alums, which crystals contain the several salts, homogeneously distributed throughout, and in any proportions. Metallic alloys, glasses, and probably dyed fibers are solid solutions.

For liquid solutions, see pp. 14, 15.

Combination of gaseous elements by volume.—The laws of definite proportions, of multiple proportions, and of reciprocal proportions (pp. 22, 23), refer to proportions *by weight* in which elements unite to form compounds.

When the proportions *by volume* in which gaseous elements combine to form compounds are compared with each other and with the volumes of the gases produced, all at the same temperature and pres-

sure, simple relations are also found to exist, which are expressed in the laws of Gay-Lussac:

First.—There exists a simple relation between the volumes of gases which combine with each other.

Second.—There exists a simple relation between the sum of the volumes of the constituent gases, and the volume of the gas formed by their union. For example:

1 volume chlorine unites with 1 volume hydrogen to form 2 volumes hydrochloric acid.

1 volume oxygen unites with 2 volumes hydrogen to form 2 volumes vapor of water.

1 volume nitrogen unites with 3 volumes hydrogen to form 2 volumes ammonia.

1 volume oxygen unites with 1 volume nitrogen to form 2 volumes nitric oxide.

1 volume oxygen unites with 2 volumes nitrogen to form 2 volumes nitrous oxide.

It will be noted that hydrogen combines with chlorine, oxygen and nitrogen in the respective proportions by volume of 1:1, 2:1 and 3:1. Also, that, while the volume of the compound of hydrogen and chlorine is equal to the sum of the volumes of the components, in the formation of the compound with oxygen there is a condensation in volume of one-third, and of that with nitrogen of one-half.

Molecular and Atomic Theories.—**Postulate of Avogadro, or of Ampère.**—In explanation of the facts just cited (as well as of many others), it is assumed that matter is not infinitely divisible, that there is a certain *smallest quantity of any substance which can exist in the free state*, which is called the **molecule**. With regard to compound substances (p. 22), this is more than a mere assumption, for, considering the smallest quantity of a compound, however small it may be, it still retains the properties of the compound, but it contains at least two smaller magnitudes, of substances whose properties differ from those of the compound, *i. e.*, those of the elements of which it is composed, and, therefore, it cannot itself be infinitely small. The molecule of hydrochloric acid contains both hydrogen and chlorine, and, however small it may be, the whole must be greater than either of its parts, and it must therefore have a definite magnitude.

Almost simultaneously, in 1811 and 1812, Avogadro and Ampère based upon the facts described in the laws of Gay-Lussac the postulate that **equal volumes of gases, under like conditions of temperature and pressure, contain equal numbers of molecules**.

This is usually referred to as the “law” of Avogadro, or of Ampère. It has, however, not the force of a scientific “law,” which, like the laws above quoted, is simply a generalized statement of a series of observed and proven facts. This statement, being based upon the undemonstrable assumption of the existence of molecules, is no more capable of proof than is the postulate of Euclid, that “a straight line may be drawn between any two points.” But this postu-

late of Avogadro has proven itself to be of enormous utility in the development of both chemistry and physics; and its close and uniform accordance with the results of both physical and chemical investigations, and with the modern kinetic theory of gases lends it additional support.

Applying the postulate of Avogadro to the laws of Gay-Lussac, we may translate the first three combinations given in the table on page 24, into the following:

- 1 molecule chlorine unites with 1 molecule hydrogen, to form 2 molecules hydrochloric acid.
- 1 molecule oxygen unites with 2 molecules hydrogen, to form 2 molecules vapor of water.
- 1 molecule nitrogen unites with 3 molecules hydrogen, to form 2 molecules ammonia.

But the ponderable quantities in which these combinations take place are:

35.5	chlorine to.....	1	hydrogen.
16	oxygen to.....	2	hydrogen.
14	nitrogen to.....	3	hydrogen.

And as single molecules of hydrogen, oxygen and nitrogen are in these combinations subdivided to form 2 molecules of hydrochloric acid, water and ammonia, it follows that these molecules must each contain two equal quantities of hydrogen, oxygen and nitrogen, less in size than the molecules themselves. And, further, as in these instances each molecule contains two of the smaller quantities, or **atoms**, the relation between the weights of the molecules must also be the relation between the weights of the atoms, and we may therefore express the combinations thus:

- 1 atom chlorine weighing 35.5 unites with 1 atom hydrogen weighing 1;
- 1 atom nitrogen weighing 16 unites with 2 atoms hydrogen weighing 2;
- 1 atom oxygen weighing 14 unites with 3 atoms hydrogen weighing 3;

and consequently, if the atom of hydrogen weighs 1, that of chlorine weighs 35.5, that of oxygen 16, and that of nitrogen 14.

Assuming, then, the existence of molecules and atoms, the distinction between them may be expressed in the following definitions:

A molecule is the smallest quantity of any substance that can exist in the free state.

An atom is the smallest quantity of an elementary substance that can enter into a chemical reaction.

The molecule is always made up of atoms, upon whose nature, number and arrangement with regard to each other, the properties of the substance depend. In an elementary substance the atoms compos-

ing the molecules are the same in kind, and usually two in number. In compound substances they are dissimilar, and vary in quantity from two in a simple compound, like hydrochloric acid, to hundreds or thousands in more complex substances.

The word atom can only be used in speaking of an elementary body, and that only while it is passing through a reaction. When liberated, atoms usually unite to form other molecules, although there are a few elements whose molecules consist of single atoms.

The term molecule applies indifferently to elements and compounds.

Atomic Weight.—The atoms of the several elements have definite relative weights; and upon the accurate determination of these all methods of quantitative chemical analysis depend. (See Stoichiometry, p. 41.) Clearly, as the atomic weights are *relative*, the weight of one atom of any element may be selected as the unit or base in terms of which the weights of the atoms of other elements may be expressed. Formerly the unit adopted was the weight of one atom of the lightest known substance, hydrogen, and the atomic weight of an element represented the weight of one atom of that element as compared with the weight of one atom of hydrogen. What the *absolute weight* of an atom of any element may be we do not know.

But the determination of the atomic weight of an element depends upon accurate analyses of compounds of that element, and hydrogen, unfortunately, forms compounds amenable to accurate analysis with but few other elements. Oxygen, on the other hand, forms compounds with a great number of other elements, and determinations of atomic weights have usually been made with reference to oxygen in the first instance. If expressed in terms of $H = 1$, therefore, their accuracy depends upon the correctness of the determination of the ratio between the atomic weights of oxygen and of hydrogen, which, according to the most recent determination, is $H : O :: 1 : 15.88$ or $O : H :: 16 : 1.008$. But this ratio cannot be considered as being definitely decided; therefore, to avoid the necessity of a recalculation of all atomic weights with increased accuracy of the determination of the ratio $O : H$, chemists have agreed that the atomic weight of oxygen be taken as the base of the system at 16. The following table contains a list of the elements at present known, with their atomic weights, calculated with $O = 16$ (known as the International Atomic Weights). It is recommended that students use the nearest integral numbers: *e. g.*, 108 for silver; 1 for hydrogen.

Molecular Weight.—We have seen (p. 25) that in the formation of hydrochloric acid, water, and ammonia, the molecules of hydrogen each contribute one-half of their material to the formation of each of the several new molecules. The molecules of hydrogen must, therefore, contain at least two atoms each; and it can also be shown that the molecules of chlorine, oxygen, nitrogen and, in fact, of most

ELEMENTS

NAME	Symbol	Atomic Weight		NAME	Symbol	Atomic Weight	
		Approximate	International (1918) O=16			Approximate	International (1918) O=16
Aluminium	Al	27	27.1	Molybdenum	Mo	96	96.0
Antimony (<i>Stibium</i>)	Sb	120	120.2	Neodymium	Nd	144	144.3
Argon	A	40	39.88	Neon	Ne	20	20.2
Arsenic	As	75	74.96	Nickel	Ni	58	58.68
Barium	Ba	137	137.37	Niton (Radium Emanation) ...	Nt	222	222.4
Bismuth	Bi	208	208.00	Nitrogen	N	14	14.01
Boron	B	11	11.0	Osmium	Os	191	190.9
Bromine	Br	80	79.92	Oxygen	O	16	16.00
Cadmium	Cd	112	112.40	Palladium	Pd	107	106.7
Cæsium	Cs	133	132.81	Phosphorus	P	31	31.04
Calcium	Ca	40	40.07	Platinum	Pt	195	195.2
Carbon	C	12	12.005	Potassium			
Cerium	Ce	140	140.25	(<i>Kalium</i>)	K	39	39.10
Chlorine	Cl	35.5	35.46	Praseodymium (<i>c</i>)	Pr	141	140.9
Chromium	Cr	52	52.0	Radium	Ra	226	226.0
Cobalt	Co	59	58.97	Rhodium	Rh	103	102.9
Columbium (<i>a</i>)...	Cb	93	93.1	Rubidium	Rb	85	85.45
Copper (<i>Cuprum</i>)	Cu	63	63.57	Ruthenium	Ru	102	101.7
Dysprosium	Dy	162	162.5	Samarium	Sa	150	150.4
Erbium	Er	168	167.7	Scandium	Sc	44	44.1
Europium	Eu	152	152.0	Selenium	Se	79	79.2
Fluorine	F	19	19.0	Silicon	Si	28	28.3
Gadolinium	Gd	157	157.3	Silver (<i>Argentum</i>)	Ag	108	107.88
Gallium	Ga	70	69.9	Sodium (<i>Natrium</i>)	Na	23	23.00
Germanium	Ge	72	72.5	Strontium	Sr	87.5	87.63
Glucinum (<i>b</i>) ...	Gl	9	9.1	Sulphur	S	32	32.06
Gold (<i>Aurum</i>) ..	Au	197	197.2	Tantalum	Ta	181	181.5
Helium	He	4	4.00	Tellurium	Te	127	127.5
Holmium	Ho	163	163.5	Terbium	Tb	159	159.2
Hydrogen	H	1	1.008	Thallium	Tl	204	204.0
Indium	In	115	114.8	Thorium	Th	232	232.4
Iodine	I	127	126.92	Thulium	Tm	168	168.5
Iridium	Ir	193	193.1	Tin (<i>Stannum</i>)...	Sn	118.5	118.7
Iron (<i>Ferrum</i>) ..	Fe	56	55.84	Titanium	Ti	48	48.1
Krypton	Kr	83	82.92	Tungsten			
Lanthanum	La	139	139.0	(<i>Wolframium</i>) .	W	184	184.0
Lead (<i>Plumbum</i>) .	Pb	207	207.26	Uranium	U	238	238.2
Lithium	Li	7	6.94	Vanadium	V	51	51.0
Lutecium	Lu	175	175.0	Xenon	Xe	130	130.2
Magnesium	Mg	24	24.32	Ytterbium (<i>d</i>) ..	Yb	173	173.5
Manganese	Mn	55	54.93	Yttrium	Yt	89	88.7
Mercury (<i>Hydrargyrum</i>)	Hg	200	200.6	Zinc	Zn	65	65.37
				Zirconium	Zr	90	90.6

(a) Also formerly known as Niobium, Nb.

(b) Also formerly known as Beryllium, Be.

(c) Also formerly known as Didymium, Di.

(d) Also known as Neoytterbium.

other elements also contain at least two atoms each. There are exceptions, however, in the cases of several metals, whose molecules consist of single atoms.

Taking the weight of one atom of hydrogen as the basis of molecular as well as of atomic weights **the molecular weight of a substance is the weight of its molecule as compared with the weight of an atom of hydrogen.** It is immaterial to this definition what the absolute weight of the hydrogen atom may be, or whether it is considered as weighing 1.000 or 1.008. The molecular weight is also, obviously, the sum of the weights of the atoms making up the molecule.

A ready method for determining the molecular weights of substances existing or obtainable in the aëriform state is based upon the postulate of Avogadro. The specific gravity of a gas or vapor referred to hydrogen is the weight of any given volume as compared with the weight of an equal volume of hydrogen (p. 3). But equal volumes contain equal numbers of molecules (p. 24), and the relation of weights, the sp. gr., of the whole is the same for any equal fractions, down to the molecules, and therefore this specific gravity is the weight of a molecule of the gas as compared with that of a molecule of hydrogen; and as the molecule of hydrogen contains two atoms, while one atom is the unit of comparison, it follows that **the specific gravity of a gas compared with hydrogen, multiplied by two, is its molecular weight.**

For example, the gas acetylene and the liquid benzene each contain 92.31 per cent. of carbon, and 7.69 per cent. of hydrogen; which is equivalent to 24 parts, or two atoms of carbon; and 2 parts, or two atoms of hydrogen. The sp. gr. of acetylene, referred to hydrogen = 2, is 13; its molecular weight is, therefore, 26, and its molecule contains two atoms of carbon and two atoms of hydrogen. The sp. gr. of vapor of benzene is 39; its molecular weight is, therefore, 78, and its molecule contains six atoms of carbon and six atoms of hydrogen.

When a substance is not capable of being volatilized, its molecular weight may be obtained from certain properties of its solutions, which will be considered in connection with organic chemistry (see p. 195).

The vapor densities of comparatively few elements are known:

	Vapor Density	Atomic Weight	Molecular Weight
Hydrogen	1	1	2
Oxygen	16	16	32
Sulphur	32	32	64
Selenium	82	79	164
Tellurium	130	128	260
Chlorine	35.5	35.5	71
Bromine	80	80	160
Iodine	127	127	254

	Vapor Density	Atomic Weight	Molecular Weight
Phosphorus	63	31	124
Arsenic	150	75	300
Nitrogen	14	14	28
Potassium	39	39	78
Cadmium	56	112	112
Mercury	100	200	200

The atomic weight being, in most of the above instances, equal to the vapor density, and to half the molecular weight, it may be inferred that *the molecules of these elements consist of two atoms*. Noticeable discrepancies exist in the case of four elements. The molecular weights of phosphorus and arsenic, as obtained from their vapor densities, are not double, but four times as great as their atomic weights. The molecules of phosphorus and arsenic are, therefore, supposed to contain four atoms. Those of cadmium, zinc and mercury contain but one atom.

Gram-molecule—Mol.—That quantity of a substance whose weight is represented by its molecular weight expressed in grams is called a **gram-molecule**, or **mol**; as 32 gms. oxygen, 70.9 gms. chlorine, 18.016 gms. water.

The mol is a quantity both theoretically and practically important. We have now to consider it in connection with certain facts already referred to.

Molecular Volume.—The molecular volume of a gas or liquid is the volume occupied by one mol of the substance under normal conditions.

According to the postulate of Avogadro (p. 24), equal molecular weights (mols) of all gases must occupy the same volume, at the same temperature and pressure, or, in other words: *the molecular volume (Vm) of gases is a constant quantity*. The molecular volume of a gas is the product of its specific volume (Vs), *i.e.*, the volume in cc. which 1 gm. occupies at 0° and 76 cm., and its molecular weight. Thus

	Weight of 1 L in gms. at 0° and 76 cm.	Vs.	Mw.	Vs×Mw, in L.
Hydrogen	0.08988.....	11,111	2.016.....	22.399
Oxygen	1.4291	699.7.....	32.000.....	22.390
Nitrogen	1.2507	799.5.....	28.080.....	22.450

The volume occupied by 1 mol of a gas at 0° and 76 cm. is 22.4 liters. Consequently the weight, *p*, of any given volume of gas, *v*, in liters, reduced to normal conditions is: $p = \frac{Mw. \times v}{22.4}$, and the volume, in liters, of any given weight of gas is: $v = \frac{22.4 p}{Mw.}$

Valence or atomicity.—It is known that the atoms of different elements possess different capacities for combining with and for replacing atoms of hydrogen. Thus:

- 1 atom of chlorine combines with 1 atom of hydrogen.
- 1 atom of oxygen combines with 2 atoms of hydrogen.
- 1 atom of nitrogen combines with 3 atoms of hydrogen.
- 1 atom of carbon combines with 4 atoms of hydrogen.

The valence, atomicity, or equivalence of an element is the saturating capacity of one of its atoms as compared with that of one atom of hydrogen.

Elements may be classified according to their valence into—

Univalent elements, or monads.....	Cl'
Bivalent elements, or dyads.....	O''
Trivalent elements, or triads.....	B'''
Quadrivalent elements, or tetrads.....	C ^{iv}
Quinivalent elements, or pentads.....	P ^v
Sexivalent elements, or hexads.....	W ^{vi}

Elements of even valence, *i. e.*, those which are bivalent, quadrivalent, or sexivalent, are sometimes called **artiads**; those of uneven valence being designated as **perissads**.

In notation the valence is indicated, as above, by signs placed to the right and above the symbol of the element.

But the valence of the elements is not fixed and invariable. Thus, while chlorine and iodine each combine with hydrogen, atom for atom, and in those compounds are consequently univalent, they unite with each other to form two compounds—one containing one atom of iodine and one of chlorine, the other containing one atom of iodine and three of chlorine. Chlorine being univalent, iodine is obviously trivalent in the second of these compounds. Again, phosphorus forms two chlorides, one containing three, the other five atoms of chlorine to one of phosphorus.

In view of these facts, we must consider either: 1, That the valence of an element is that which it exhibits in its most saturated compounds, as phosphorus in the pentachloride, and that the lower compounds are non-saturated, and have free valences; or 2, that the valence is variable. The first supposition depends too much upon the chances of discovery of compounds in which the element has a higher valence than that which might be considered the maximum to-day. The second supposition—notwithstanding the fact that, if we admit the possibility of two distinct valences, we must also admit the possibility of others—is certainly the more tenable and the more natural. *In speaking, therefore, of the valence of an element, we must not consider it as an absolute quality of its atoms, but simply as their combining capacity in the particular class of compounds under consideration.* Indeed, compounds are known in whose molecules the atoms of one element exhibit two distinct valences. Thus, ammonium cyanate ($\text{H}_4\equiv\text{N}-\text{O}-\text{C}\equiv\text{N}$) contains two atoms of nitrogen: one in the ammonium group is quinivalent, one in the acid radical is trivalent.

TABLE OF THE VALENCES OF SOME OF THE COMMONER ELEMENTS AND RADICALS.

Univalent	Bivalent	Trivalent	Quadrivalent	Quinivalent	Sexivalent
H	O	N	C	N	S
F	S	P	Si	P	W
Cl	Mn (ous)	As	S	As	
Br	Fe (ous)	Sb	Pt	Sb	
I	Pb	B	Sn (ic)		
Li	Sn (ous)	Fe (ic)			
Na	Ca	Bi			
K	Ba	Al			
Ag	Mg				
Cu (ous)	Zn	(PO ₄)			
Hg (ous)	Cu (ic)				
	Hg (ic)				
(OH)					
(NO ₃)	(SO ₄)				
(NH ₄)	(CO ₃)				
(CN)					
(C ₂ H ₃ O ₂)					

The chemical equivalent, or equivalent weight, of an element is the weight of that element capable of combining with unit weight of hydrogen (or chlorine). It is, therefore, its atomic weight divided by its valence. We have seen (p. 25) that 35.5 parts by weight of chlorine combine with 1 part by weight of hydrogen, 16 of oxygen with 2 of hydrogen, and 14 of nitrogen with 3 of hydrogen. Chlorine being univalent, oxygen bivalent and nitrogen trivalent, their equivalent weights are, therefore, respectively: $35.5 \div 1 = 35.5$, $16 \div 2 = 8$, and $14 \div 3 = 4.67$. (See also p. 37.)

A gram-equivalent of an element is a quantity of that element whose weight in grams is equal to its molecular weight divided by its valence. Thus 23 gms. of sodium, and $65.4 \div 2 = 32.7$ gms. of zinc, are gram equivalents of those metals.

Symbols, Formulæ, Equations.—Symbols are conventional abbreviations of the names of the elements; they consist of the initial letter of the Latin name of the element, to which is usually added one of the other letters. If there are more than two elements whose names begin with the same letter, the single-letter symbol is reserved for the commonest element. Thus, we have ten elements whose names begin with C; of these the commonest is Carbon, whose symbol is C; the others have double-letter symbols, as Chlorine, Cl; Cobalt, Co; Copper, Cu (Cuprum), etc.

These symbols do not indicate simply an indeterminate quantity, but represent one atom of the corresponding element.

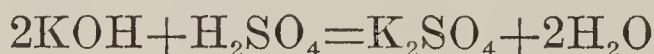
When more than one atom is spoken of, the number of atoms which it is desired to indicate is written either before the symbol or, in small figures, after and below it. Thus, H indicates one

atom of hydrogen; 2Cl, two atoms of chlorine; C₄, four atoms of carbon, etc.

What the symbol is to the element, the **formula** is to the compound. By it the number and kind of atoms of which the molecule of a substance is made up are indicated. The simplest kind of formulæ are what are known as **empirical formulæ**, which indicate only the kind and number of atoms which form the compound. Thus, HCl indicates a molecule composed of one atom of hydrogen united with one atom of chlorine; 5H₂O, five molecules, each composed of two atoms of hydrogen and one atom of oxygen, the number of molecules being indicated by the proper numeral placed before the formula, in which place it applies to all the symbols following it. Sometimes it is desired that a numeral shall apply to a part of the symbols only, in which case they are enclosed in parentheses; thus, Al₂(SO₄)₃ means twice Al and three times SO₄.

For other varieties of formulæ, see pp. 47, 48.

Equations are combinations of formulæ and algebraic signs so arranged as to indicate a chemical reaction and its results. The signs used are the plus and equality signs; the former being equivalent to "and," and the second meaning "have reacted upon each other and have produced." The substances entering into the reaction are placed before the equality sign, and the products of the reaction after it; thus, the equation



means, when translated into ordinary language: two molecules of potassium hydroxide, each composed of one atom of potassium, one atom of hydrogen, and one atom of oxygen, *and* one molecule of sulphuric acid, composed of two atoms of hydrogen, one atom of sulphur, and four atoms of oxygen, *have reacted upon each other and have produced* one molecule of potassium sulphate, composed of two atoms of potassium, one atom of sulphur, and four atoms of oxygen, *and* two molecules of water, each composed of two atoms of hydrogen and one atom of oxygen.

As no material is ever lost or created in a reaction, the number of each kind of atom occurring before the equality sign in an equation must always be the same as that occurring after it. In writing equations, they should always be proved by examining whether the half of the equation before the equality sign contains the same number of each kind of atom as that after the equality sign. If it does not, the equation is incorrect.

The word **reaction** is used in chemistry with two distinct meanings: As applying to the action mentioned above, it refers to the mutual action of two substances upon each other. In the other meaning it refers to the action of substances upon certain organic pigments. Thus, the **reaction** of a substance is **acid**, when it turns

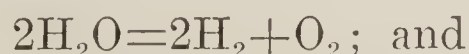
blue litmus red; **alkaline**, when it turns reddened litmus blue; **amphoteric**, when it turns red litmus blue and blue litmus red; and **neutral**, when it has no action upon either blue or red litmus.

Chemical reactions in the former sense are either:

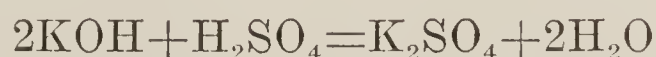
1. **Combinations**, also called **syntheses**, in which elements or simpler compounds unite to form more complex molecules, as when



2. **Decompositions**, also called **analyses**, processes the reverse of combinations, as when



3. **Double decompositions**, or **metatheses**, when two substances mutually react upon each other with formation of new substances, as when



When one of the reagents in a double decomposition is water, the process is called **hydrolysis** (see p. 64).

Special varieties of these several kinds of reaction, which are sufficiently distinctive, have received distinguishing names, such as condensations, etc., and will be considered later. There also occur, notably with the compounds of carbon, instances of

(4) **Atomic rearrangement**, or **transposition**, in which the composition remains the same, but the constitution (p. 46) is changed: as when ammonium isocyanate, $\text{O}:\text{C}:\text{N}.\text{NH}_4$ is converted into urea, $\text{H}_2.\text{NCO}.\text{NH}_2$.

Electrolysis.—We have seen (p. 20) that when hydrochloric acid is electrolyzed, hydrogen is given off at the negative pole, and is therefore electropositive, while chlorine is given off at the positive pole, and is therefore electronegative. But if a compound of chlorine and sulphur is electrolyzed, chlorine is given off at the negative electrode, and is therefore electropositive. Chlorine is consequently electropositive to sulphur, and electronegative to hydrogen.

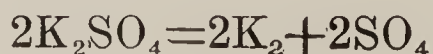
The results of electrolysis of binary compounds of many elements have shown that oxygen is electronegative, and the alkali metals (p. 149) are electropositive to all other elements with which they form binary compounds. If the elements are arranged in an **electrochemical series**, with oxygen at the electronegative end and caesium at the electropositive end, and if the other elements are placed in the series in such positions that each will be between oxygen and all other elements toward which it is electronegative, it will be found that hydrogen will occupy a position about midway between the two ends, but nearer to the electronegative, and that the elements of the acidulous class (p. 52) will be placed between hydrogen and oxygen, while the metals will be placed to the electropositive side of

hydrogen. See the accompanying arrangement in the shape of a horseshoe.

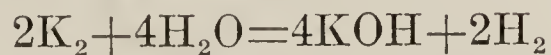
ELECTRONEGATIVE	ELECTROPOSITIVE
Oxygen	Cæsium
Sulphur	Rubidium
Nitrogen	Potassium
Fluorine	Sodium
Chlorine	Lithium
Bromine	Barium
Iodine	Strontium
Selenium	Calcium
Phosphorus	Magnesium
Arsenic	Beryllium
Chromium	Yttrium
Vanadium	Erbium
Molybdenum	Aluminium
Tungsten	Zirconium
Boron	Thorium
Carbon	Cerium
Antimony	Didymium
Tellurium	Lanthanum
Tantalum	Manganese
Columbium	Zinc
Titanium	Iron
Silicon	Nickel
Hydrogen	Cobalt
Gold	Thallium
Osmium	Cadmium
Iridium	Lead
Platinum	Indium
Rhodium	Tin
Ruthenium	Bismuth
Palladium	Uranium
Mercury	Copper
Silver	

Arbitrarily, elements electronegative to hydrogen are considered as electronegative elements, those electropositive to hydrogen as electropositive elements.

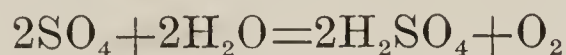
A similar separation takes place in the electrolysis of compounds containing more than two elements, one element being liberated at one pole and the remaining group of elements separating at the other. This **primary decomposition** is generally modified, as to its final products, by subsequent chemical reactions, called **secondary actions**. When, for example, a solution of potassium sulphate is electrolyzed, the liquid surrounding the positive electrode becomes acid in reaction, and gives off oxygen. At the same time the liquid at the negative side becomes alkaline, and gives off a volume of hydrogen double that of the oxygen liberated. In the first place potassium sulphate, which consists of potassium, sulphur and oxygen, yields on primary separation electropositive potassium, which separates at the negative pole; and, an electronegative group of sulphur and oxygen, which goes to the positive pole:



The potassium liberated immediately decomposes the surrounding water, forming caustic potash, to which the alkaline reaction is due, and hydrogen, which is liberated:



The sulphur-oxygen group at the positive pole also immediately reacts with water to form sulphuric acid, and oxygen is liberated:



one molecule of oxygen being liberated for every two of hydrogen.

The name **ion** was first applied by Faraday to the primary products of electrolysis; and those which separate at the positive electrode, or anode, are called **anions**, while those which separate at the negative electrode, or cathode, are called **cations**. Thus, potassium sulphate yields the cation K, and the anion SO₄. Cations are designated by the plus sign, anions by the minus sign. Thus:

$K_2SO_4=K^+K^+SO_4^-$, or, better, the cations, as well as their valences, are designated by the proper number of dots placed after the symbol, thus, H[·], Ca^{··} and the anions similarly by prime marks, thus, OH', SO₄'', and AsO₄'''. *Hydrogen, the metals, and basic radicals are cations; hydroxyl and the acid residues are anions.* The residues of acids are **compound ions**, that is, ions consisting of more than one element.

According to the earlier views of electrolysis, the decomposition of the molecule into its ions was considered to be a result of the action of the galvanic current. According to the theory of Arrhenius, **dissociation** into ions, or **ionization**, occurs when the electrolyte is dissolved. A solution of potassium chloride contains not only the molecular KCl, but also the cation K[·] and the anion Cl', and the action of the current is to separate these, already liberated, ions at the respective electrodes. It is assumed that the hydrogen and metallic ions are charged with positive electricity, and the hydroxyl and acid-residue ions with negative electricity, and therefore the former are attracted to the negatively charged cathode, and the latter to the positively charged anode.

We have seen that when an aqueous solution of an acid is electrolyzed, hydrogen is always given off at the cathode. Although hydrogen exists in innumerable compounds other than acids, it is only from them that it is so separated, and only from them when in solution. That this hydrogen does not originate from the water is shown by the fact that perfectly pure water is neither a conductor nor an electrolyte. It is only in solutions of acids (or in solutions of acid salts or esters, which still retain acid properties), therefore, that hydrogen exists in the ionized form, **hydrion**. Hydrion also differs from molecular or atomic hydrogen in other respects. It is only known in solution, while molecular hydrogen is almost insoluble in

water. It reddens litmus and is replaceable by metals, properties not possessed by either atomic or molecular hydrogen. Similarly, when solutions of bases are electrolyzed hydroxyl, OH, is always produced as a primary product at the anode. And, here again, although hydroxyls exist in many compounds other than those having basic properties, it is only from solutions of these that hydroxyl is thus separated, as only their solutions contain the ion, **hydroxidion**. And hydroxidion differs further from hydroxyl in that it is only known in solution, that it blues reddened litmus, and that it is replaceable by acid residues.

In the electrolysis of an oxyacid (see below) that group which is primarily separated at the positive electrode is called the **residue** of the acid. (See p. 46.)

Acids, Bases and Salts.—All ternary and quaternary mineral substances have one of three functions. The **function** of a substance is its chemical character and relationship, and indicates certain general properties, reactions and decompositions which all substances having the same function possess and undergo alike. Thus in mineral chemistry we have **acids, bases and salts**; and in organic chemistry, **alcohols, aldehydes, acids, ketones, esters, etc.**

An acid is a compound of an electronegative element or residue with hydrogen, which hydrogen it can part with in exchange for an electropositive element, without formation of a base. An acid has also been defined as a compound body which evolves water by its action upon pure caustic soda or potash. This latter definition is undesirable in view of the existence of certain zinc and aluminium compounds (pp. 175, 178). No substance which does not contain hydrogen can, therefore, be called an acid. An acid has also been defined as a compound yielding hydrion on electrolysis.

The basicity of an acid is the number of replaceable hydrogen atoms in its molecule.

A **monobasic** acid is one containing a single replaceable atom of hydrogen, as nitric acid, HNO_3 ; a **dibasic** acid is one containing two such replaceable atoms, as sulphuric acid, H_2SO_4 ; a **tribasic** acid is one containing three replaceable hydrogen atoms, as phosphoric acid, H_3PO_4 . **Polybasic** acids are such as contain more than one atom of replaceable hydrogen.

Hydracids are acids containing no oxygen; **oxyacids** contain both hydrogen and oxygen.

The term **base** is regarded by many authors as applicable to any compound body capable of neutralizing an acid. It is, however, more consistent with modern views to limit the application of the name to such ternary compound substances as are capable of entering into double decomposition with acids to form salts and water. They may be considered as one or more molecules of water in which one-half of the hydrogen has been replaced by an electropositive element

or radical; or as compounds of such elements or radicals with one or more groups, OH. Being thus considered as derivable from water, they are also known as **hydroxides**. They have the general formula, $M_n(\text{OH})_n$. They are **monatomic**, **diatomic**, **triatomic**, etc., according as they contain one, two, three, etc., groups **oxhydryl**, or **hydroxyl** (OH). As acids having one, two or three, etc., atoms of replaceable hydrogen are designated as monobasic, dibasic, or tribasic acids, etc., so bases having one replaceable hydroxyl are spoken of as **monacid bases**, those having two as **diacid bases**, etc. A base has also been defined as a compound yielding hydroxidion on electrolysis.

The **atomicity** of a compound is the number of hydroxyls in its molecule, which it may lose by their combination with the hydrogen of acids. Bases are said to be **monatomic**, **monohydric** or **monacid**; **diatomic**, **dihydric** or **diacid**, etc., according as the number of their hydroxyls is one, two, etc.

A **double decomposition** is a reaction in which both of the reacting compounds are decomposed to form two new compounds.

Thiobases, or **hydrosulphides**, are compounds in all respects resembling the bases, except that in them the oxygen is replaced by sulphur.

An **equivalent** of an acid or base is a quantity thereof equal to one molecule, divided by the basicity or acidity; or that proportionate quantity of its molecular weight which contains only one basic hydrogen atom or only one acid displaceable hydroxyl. Thus, a molecule and an equivalent of potassium hydroxide, KOH, both weigh 56.11; a molecule of sulphuric acid, H_2SO_4 , weighs 98.08, and an equivalent 49.04.

A **gram-equivalent** (gm:eq.) of any substance is a quantity thereof whose weight is that of its equivalent, expressed in grams.

Concentration.—By the “concentration” or “strength” of a solution is understood the amount of the solute in unit volume of the solution (not of the solvent). Various units are used for the expression of concentration:

In **percentage solutions**, strictly, both solvent and solute are taken in parts by weight. Thus, a 4 per cent. solution of sodium chloride is made with 4 gms. NaCl and 96 gms. H_2O . **Volume: per cent. solutions** are usually more convenient: A 4 per cent. solution of sodium chloride is made by dissolving 4 gms. NaCl in a volume of water such that the finished solution measures 100 cc. The difference between per cent. and v per cent. solutions is more marked with solvents other than water. While per cent. solutions are independent of temperature, v per cent. solutions have the concentration indicated only at the temperature for which they are made, which is usually 18°C .

Normal solutions are of two kinds: **Molecular-normal**, which

contain one gram-molecule in a liter of solution, and **Equivalent-normal**, which contain one gram-equivalent in a liter. Thus, one liter of M-N solution of sulphuric acid contains 98 gms. H_2SO_4 , and one liter of Eq-N solution 49 gms. Usually "normal" solutions are molecular-normal, except solutions used in volumetric analysis, which are equivalent-normal, whole or fractional. **Decinormal solutions** $\left(\frac{N}{10}\right)$ contain $\frac{1}{10}$ gm:mol. or gm:eq. per liter, etc. **Standard solutions** are solutions of some fixed volume-concentration, which may be of any value desired for the use intended.

Salts are substances formed by the substitution of electro-positive, or basylous, elements for a part or all of the replaceable hydrogen of acids. They are formed, therefore, when bases and acids enter into double decomposition.

As salts are produced by double decomposition between acids and bases, the latter play as much part in the formation of salts as do the former, and we may also consider the salts as substances formed by the substitution of acid residues (p. 46) for a part or all of the hydroxyl of bases. Salts have also been defined as compounds formed by the union of the anion of an acid and the cation of a base.

It will be seen from the above that in some salts the hydrogen of the acid is only partly replaced, as in baking soda: $\text{OC} \begin{smallmatrix} \text{ONa} \\ \text{OH} \end{smallmatrix}$. Such salts are called **bi salts** or **acid salts**. There exist, also, salts in which a portion of the hydroxyl of the bases is retained. Such salts are called **basic salts**, *e. g.*, basic lead nitrate NO_3PbOH . (See p. 45.)

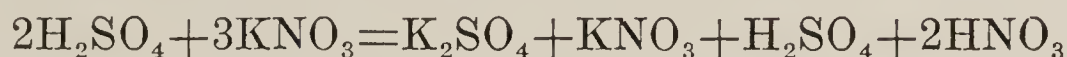
The term **salt**, as used at present, applies to the compounds formed by the substitution of a basylous element for the hydrogen of *any* acid; and indeed, as used by some authors, to the acids themselves, which are considered as salts of hydrogen. It is probable, however, that eventually the name will be limited to such compounds as correspond to acids whose molecules contain more than two elements. Indeed, from the earliest times of modern chemistry a distinction has been observed between the **haloid salts**, *i. e.*, those the molecules of whose corresponding acids consist of hydrogen, united with one other element, on the one hand; and the **oxysalts**, the salts of the oxyacids, *i. e.*, those into whose composition oxygen enters, on the other hand. This distinction, however, has gradually fallen into the background, for the reason that the methods and conditions of formation of the two kinds of salts are usually the same *when the basylous element belongs to that class usually designated as metallic*.

There are, however, important differences between the two classes of compounds. There exist compounds of all of the elements corresponding to the hydracids, binary compounds of chlorine, bromine, iodine and sulphur. There is, on the other hand, a large class of elements the members of which are incapable of forming salts corre-

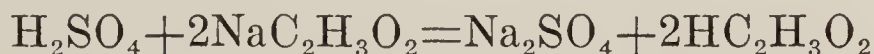
sponding to the oxyacids. No salt of an oxyacid with any one of the elements usually classed as metalloids (excepting hydrogen) has been obtained.

Haloid salts may be formed by direct union of their constituent elements; oxysalts are never so produced.

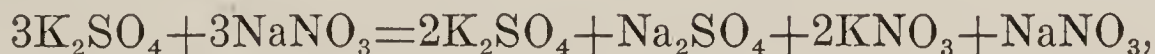
Action of Acids and Bases on Salts, and of Salts on each other.—(1) If an acid is added to a solution of a salt whose acid it nearly equals in chemical activity, the salts of both acids and the acids themselves will probably exist in the solution, provided both acids and salts are soluble. Thus, if sulphuric acid is added to a solution of potassium nitrate, the solution will contain potassium sulphate and nitrate, and sulphuric and nitric acid:



(2) If an acid is added to a solution of a salt whose acid it greatly exceeds in activity, the salt is decomposed, with formation of the salt of the stronger acid, and liberation of the weaker acid, both salts and acids being soluble. Thus, if sulphuric acid is added to a solution of sodium acetate, the solution will contain sodium sulphate and acetic acid:



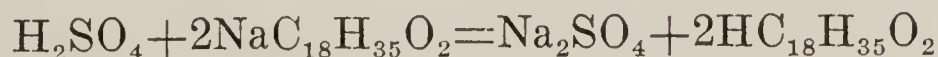
(3) When solutions of two salts, the acids of both of which form soluble salts with both bases, are mixed the resultant liquid contains the four salts. Thus, if potassium sulphate and sodium nitrate are dissolved in the same solution it will contain potassium and sodium sulphates and potassium and sodium nitrates:



or in some other proportion.

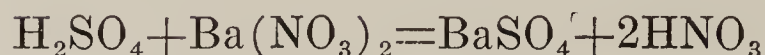
In the light of the hypothesis of ionization, the statements 1, 2 and 3, while applying to that portion of the compounds which remain un-ionized, may be better expressed in the one: Solutions of acids, bases and salts contain all the free ions. Thus, in the example given in 3, the solution contains K, Na, SO₄, and NO₃.

(4) If to a solution of a salt, whose acid is insoluble in the solvent used, an acid is added, capable of forming a soluble salt with the basylous element, such soluble salt is formed and the acid is deposited. Thus, if sulphuric acid is added to an aqueous solution of sodium stearate, stearic acid will be deposited and sodium sulphate formed:

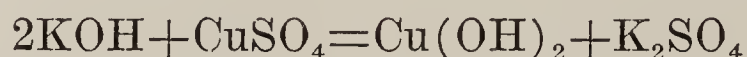


(5) If to a solution of a salt an acid is added which is capable of forming an insoluble salt with the base, such insoluble salt is formed and precipitated. Thus, if sulphuric acid is added to a solu-

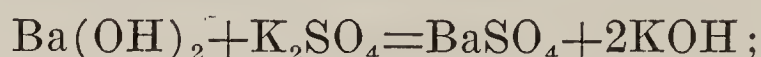
tion of barium nitrate, barium sulphate is precipitated and nitric acid liberated:



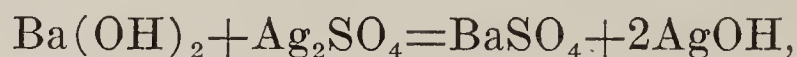
(6) If to a solution of a salt whose basylous element is insoluble a soluble base is added, capable of forming a soluble salt with the acid, such soluble salt is formed, with precipitation of the insoluble base. Thus, if potassium hydroxide is added to a solution of cupric sulphate, cupric hydroxide is precipitated and potassium sulphate formed:



(7) If a base is added to a solution of a salt with whose acid it is capable of forming an insoluble salt, such insoluble salt is formed and precipitated, and the base of the original salt, if insoluble, is also precipitated. Thus if solutions of barium hydroxide and of potassium sulphate are mixed, barium sulphate is precipitated and the solution contains potassium hydroxide:

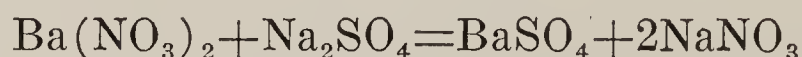


or if solutions of barium hydroxide and silver sulphate are mixed both barium sulphate and silver hydroxide will be precipitated:



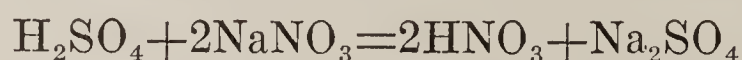
and if the substances are used in the proportions given in the equation pure water will remain.

(8) If solutions of two salts, the acid of one of which is capable of uniting with the base of the other to form an insoluble salt, are mixed, such insoluble salt is precipitated. Thus, if solutions of barium nitrate and of sodium sulphate are mixed, barium sulphate is precipitated and sodium nitrate formed:



The statements 4 to 8 may be summarized in the statement: When solutions of acids, bases or salts any of whose ions are capable of uniting to form an insoluble compound are mixed, such insoluble compound is formed and precipitated.

(9) If to a salt whose acid is volatile at the existing temperature an acid capable of forming with the basylous element a salt fixed at the same temperature is added, the fixed salt is formed and the volatile acid expelled. Thus, with the application of heat, sulphuric acid expels nitric acid from sodium nitrate to form sodium sulphate:



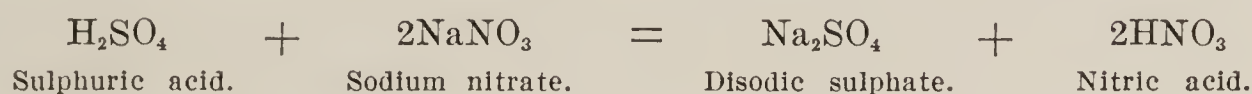
(10) Similarly, a volatile base is expelled from its salts by a fixed one. Thus potassium hydroxide and ammonium chloride form ammonia, water and potassium chloride:



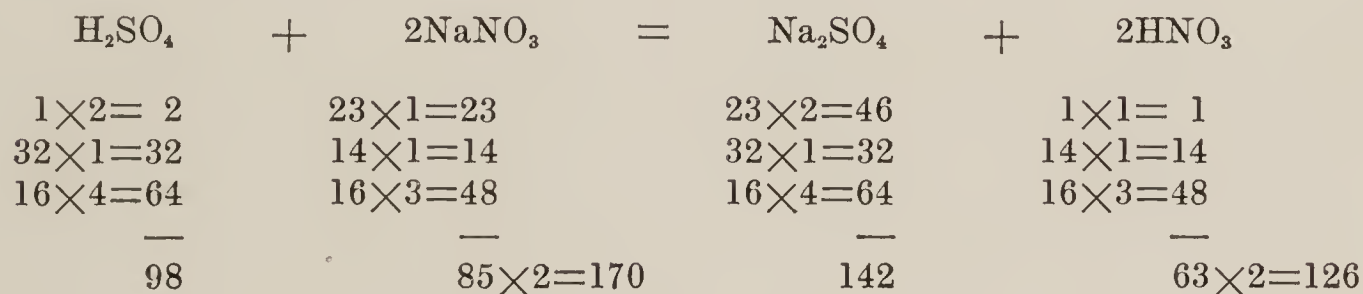
Stoichiometry in its strict sense refers to the law of definite proportions, and to its applications. In a wider sense, the term applies to the **mathematics of chemistry**, *i. e.*, to those mathematical calculations by which the quantitative relations of substances acting upon each other, and of the products of such reactions are determined.

A chemical reaction can always be expressed by an equation, which, as it represents not only the nature of the materials involved, but also the number of molecules of each, is a quantitative as well as a qualitative statement.

Let it be desired to determine how much sulphuric acid will be required to completely decompose 100 parts of sodium nitrate, and what will be the nature and quantities of the products of the decomposition. First the equation representing the reaction is constructed:



which shows that one molecule of sulphuric acid decomposes two molecules of sodium nitrate, with the formation of one molecule of sodium sulphate and two of nitric acid. The quantities of the different substances are, therefore, represented by their molecular weights, or some multiple thereof, which are in turn obtained by adding together the atomic weights of the constituent atoms:



Consequently, 98 parts H_2SO_4 decompose 170 parts NaNO_3 , and produce 142 parts Na_2SO_4 , and 126 parts HNO_3 . To find the result as referred to 100 parts NaNO_3 , we apply the simple proportion:

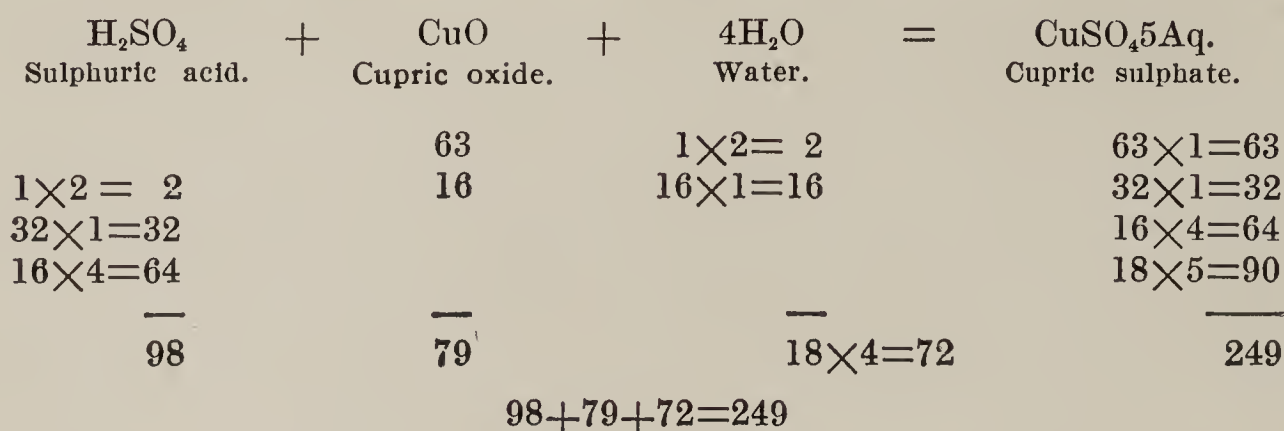
$$\begin{array}{l} 170 : 100 :: 98 : 57.64 - 57.64 = \text{parts } \text{H}_2\text{SO}_4 \text{ required.} \\ 170 : 100 :: 142 : 83.53 - 83.53 = \text{ " } \text{Na}_2\text{SO}_4 \text{ produced.} \\ 170 : 100 :: 126 : 74.11 - 74.11 = \text{ " } \text{HNO}_3 \text{ " } \end{array}$$

As in writing equations, the work should always be proved by adding together the quantities on each side of the equality sign, which should equal each other: $98 + 170 = 268 = 142 + 126 = 268$, or $57.64 + 100 = 157.64 = 83.53 + 74.11 = 157.64$.

In determining quantities as above, regard must be had to the purity of the reagents used, and, if they be crystallized, to the amount of water of crystallization (see p. 8) they contain.

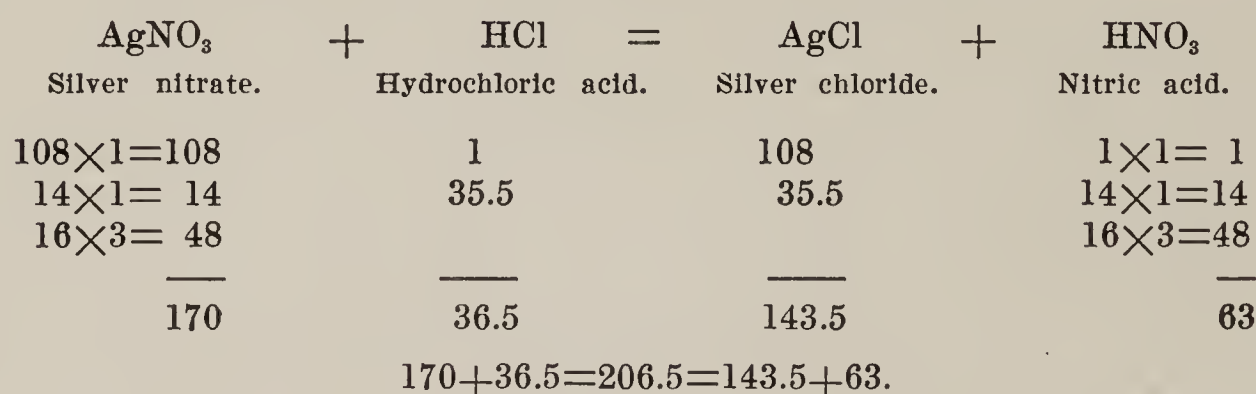
Let it be desired to determine how much crystallized cupric sulphate can be obtained from 100 parts of sulphuric acid of 92 per

cent. strength. As cupric sulphate crystallizes with five molecules of water of crystallization the reaction occurs according to the equation:



98 parts of 100 per cent. H_2SO_4 will produce, therefore, 249 parts of crystallized cupric sulphate. But as the acid liquid used contains only 92 parts of true H_2SO_4 , in 100; 100 parts of such acid will yield 233.75 parts of crystallized sulphate, for $98:92::249:233.75$.

Let the problem be to determine what percentage of silver is contained in a silver coin. Advantage is taken of the formation of the insoluble silver chloride. A piece of the coin is chipped off and weighed: weight of coin used = 2.5643 grams. The chip is then dissolved in nitric acid, forming a solution of silver nitrate. From this solution the silver is precipitated as chloride, by the addition of hydrochloric acid, according to the equation:



The silver chloride is collected, dried and weighed:

Weight of coin used.....	2.5643 grams.
Weight of AgCl obtained.....	3.0665 “

as 143.5 grams AgCl contain 108 grams Ag— $143.5:108::3.0665:2.3078$ —2.5643 grams of the coin contain 2.3078 grams of silver or 90 per cent.— $2.5643:100::2.3078:90$.

Nomenclature.—The names of the elements are mostly of Greek derivation, some are of Latin origin; some of Gothic origin and others are derived from modern languages. Very little system has been followed in naming the elements, beyond applying the termination *ium* to the metals, and *in* or *on* to the non-metals; and even to this rule there are exceptions, such as a metal called *manganese* and a non-metal called *sulphur*.

The names of *compound substances* were formerly chosen upon the same system, or rather lack of system, as those of the elements. So long as the number of compounds remained small, the use of these fanciful appellations gave rise to comparatively little inconvenience. In these later days, however, when the number of compounds known to exist, or whose existence is shown by approved theory to be possible, is practically infinite, some systematic method of nomenclature has become absolutely necessary.

The principle of the system of nomenclature at present used is that the name shall convey the composition and character of the substance.

Compounds consisting of two elements, or of an element and a radical only, *binary compounds*, are designated by compound names made up of the name of the more electropositive, followed by that of the more electronegative, in which the termination *ide* has been substituted for the termination *in*, *on*, *ogen*, *ygen*, *orus*, *ium*, and *ur*. For example: the compound of potassium and chlorine is called potassium *chloride*, that of potassium and oxygen potassium *oxide*, that of potassium and phosphorus potassium *phosphide*.

In a few instances the older name of a compound is used in preference to the one which it should have under the above rule; such are *ammonia*, NH_3 ; *water*, H_2O .

When, as frequently happens, two elements unite with each other to form more than one compound, these are usually distinguished from each other by prefixing to the name of the element varying in amount the Greek numeral corresponding to the number of atoms of that element, as compared with a *fixed* number of atoms of the other element.

Thus, in the series of compounds of nitrogen and oxygen, most of which contain two atoms of nitrogen, N_2 is the standard of comparison, and consequently the names are as follows:

N_2O	=Nitrogen <i>monoxide</i> .
$\text{NO} (= \text{N}_2\text{O}_2)$	=Nitrogen <i>dioxide</i> .
N_2O_3	=Nitrogen <i>trioxide</i> .
$\text{NO}_2 (= \text{N}_2\text{O}_4)$	=Nitrogen <i>tetroxide</i> .
N_2O_5	=Nitrogen <i>pentoxide</i> .

Another method of distinguishing two compounds of the same two elements consists in terminating the first word in *ous* in that compound which contains the less proportionate quantity of the more electronegative element, and in *ic* in that containing the greater portion; thus:

SO_2	=Sulphurous oxide.
SO_3	=Sulphuric oxide.

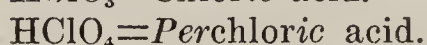
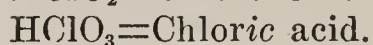
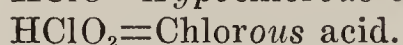
HgCl	=Mercurous chloride.
HgCl_2	=Mercuric chloride.

This method, although used to a certain extent in speaking of compounds composed of two elements of Class III (see p. 52), is used chiefly in speaking of binary compounds of elements of different classes.

In naming the *oxyacids* the word *acid* is used, preceded by the name of the electronegative element other than oxygen, to which a prefix or suffix is added to indicate the degree of oxidation. If there are only two, the least oxidized is designated by the suffix *ous*, and the more oxidized by the suffix *ic*, thus:

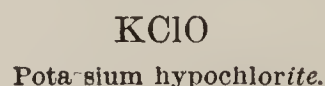
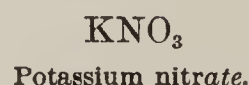
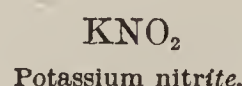
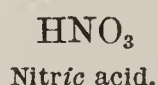


If there are more than two acids, formed in regular series, the least oxidized is designated by the prefix *hypo* and the suffix *ous*; the next by the suffix *ous*; the next by the suffix *ic*; and the most highly oxidized by the prefix *per* and the suffix *ic*; thus:



Certain elements, such as sulphur and phosphorus, exist in acids which are derived from those formed in the regular way, and which are specially designated.

The names of the *oxysalts* are derived from those of the acids by dropping the word *acid*, changing the termination of the other word from *ous* into *ite*, or from *ic* and *ate*, and prefixing the name of the electropositive element or radical; thus:



Acids whose molecules contain more than one atom of replaceable hydrogen are capable of forming more than one salt with electropositive elements, or radicals, whose valence is less than the basicity of the acid. Ordinary phosphoric acid, for instance, contains in each molecule three atoms of basic hydrogen, and consequently is capable of forming three salts by the replacement of one, two, or three of its hydrogen atoms, by one, two, or three atoms of a univalent metal. To distinguish these the Greek prefixes *mono*, *di*, and *tri* are used, the termination *ium* of the name of the metal being changed to *ic*, thus:

$\text{H}_2\text{KPO}_4 = \text{Monopotassic phosphate.}$

$\text{HK}_2\text{PO}_4 = \text{Dipotassic phosphate.}$

$\text{K}_3\text{PO}_4 = \text{Tripotassic phosphate.}$

The first is also called *dihydropotassic* phosphate, and the second, *hydrodipotassic* phosphate.

In the older works, salts in which the hydrogen has not been entirely displaced were sometimes called **bisalts** (*e.g.*, bicarbonates), or **acid salts**; those in which the hydrogen has been entirely displaced being designated as **neutral salts**, or **normal salts**.

Some elements, such as mercury, copper, and iron, form two distinct series of salts. These are distinguished, in the same way as the acids, by the use of the suffix *ous* in the names of those containing the less proportion of the electronegative group, and the suffix *ic* in those containing the greater proportion, *e. g.*:

$\text{Cu}_2\text{SO}_4 \dots\dots\dots (1\text{SO}_4:2\text{Cu}) = \text{Cuprous sulphate.}$

$\text{CuSO}_4 \dots\dots\dots (2\text{SO}_4:2\text{Cu}) = \text{Cupric sulphate.}$

$\text{FeSO}_4 \dots\dots\dots (2\text{SO}_4:2\text{Fe}) = \text{Ferrous sulphate.}$

$\text{Fe}_2(\text{SO}_4)_3 \dots\dots\dots (3\text{SO}_4:2\text{Fe}) = \text{Ferric sulphate.}$

The names, **basic salts**, **subsals** and **oxysalts** have been applied indifferently to salts, such as the lead subacetates, which are compounds containing the normal acetate and the hydroxide or oxide of lead; and to salts such as the so-called bismuth subnitrate, which is a nitrate, not of bismuth, but of the univalent radical, bismuthyl ($\text{Bi}'''\text{O}''$)'.

By **double salts** are meant such as are formed by the substitution of different elements or radicals for two or more atoms of replaceable hydrogen of the acid, such as ammonium magnesium phosphate, $\text{PO}_4\text{Mg}''(\text{NH}_4)'$.

In naming the cations, the termination *ion* is added to the stem of the name of the metal, the Latin name, if it exists, being used; but *sodion*, not *natrion*, and *potassion*, not *kalion*. Ionized hydrogen is called *hydrion*. The names of the anions are derived from those of the corresponding salts by changing the terminations from *ide* to *idion*, *e. g.*, $\text{S}'' = \text{sulphidion}$; *ite* to *osion*, *e. g.*, $\text{SO}_3'' = \text{sulphosion}$; and *ate* to *anion*, *e. g.*, $\text{SO}_4'' = \text{sulphanion}$; except CO_3'' is called *carbanion*. The anion OH' is called *hydroxidion*. When ions of different valence are derived from the same substance they are distinguished by the corresponding Greek numerals. Thus the electrolysis of H_2SO_4 proceeds in two stages, first $\text{H}_2\text{SO}_4 = \text{H}' \mid \text{HSO}_4' = \text{monosulphanion}$, then $\text{HSO}_4 = \text{H}' \mid \text{SO}_4'' = \text{disulphanion}$.

Radicals.—Many compounds contain groups of atoms which pass from one compound to another, and, in many reactions, behave like elementary atoms. Such groups are called **radicals**, or **compound radicals**.

Marsh gas has the composition CH_4 . By acting upon it in suitable ways we can cause the atom of carbon, accompanied by three of the hydrogen atoms, to pass into a variety of other compounds, such as $(\text{CH}_3)\text{Cl}$, $(\text{CH}_3)\text{OH}$, $(\text{CH}_3)_2\text{O}$, $\text{C}_2\text{H}_3\text{O}_2(\text{CH}_3)$. Marsh gas, therefore, consists of the radical (CH_3) combined with an atom of hydrogen: $(\text{CH}_3)'\text{H}$.

It is especially among the compounds of carbon that the existence of radicals comes into prominent notice. They, however, occur in inorganic substances also. Thus the nitric acid molecule consists of the radical NO_2 , combined with the group OH .

Like the elements, the radicals possess different valences, depending upon the number of unsatisfied valences which they contain. Thus the radical (CH_3) is univalent, because three of the four valences of the carbon atom are satisfied by atoms of hydrogen, leaving one free valence. The radical (PO) of phosphoric acid is trivalent, because two of the five valences of the phosphorus atom are satisfied by the two valences of the bivalent oxygen atom, leaving three free valences.

In notation the radicals are usually enclosed in brackets as above, to indicate their nature. The names of univalent radicals terminate in *yl* or in *gen*; thus: (CH_3) =methyl; (CN) =cyanogen.

The terms *radical* and *residue* are not synonymous. In speaking of acids their *radicals* are obtained by the subtraction of a number of hydroxyls equal to the basicity of the acid. Thus $\text{HNO}_3 - \text{HO} = \text{NO}_2$; $\text{H}_2\text{SO}_4 - 2\text{HO} = \text{SO}_2$; $\text{H}_3\text{PO}_4 - 3\text{HO} = \text{PO}$. The *residue* is that which remains after removal of the basic, or replaceable, hydrogen. Thus: $\text{HNO}_3 - \text{H} = \text{NO}_3$; $\text{H}_2\text{SO}_4 - \text{H}_2 = \text{SO}_4$; $\text{H}_3\text{PO}_4 - \text{H}_3 = \text{PO}_4$ (See Electrolysis, p. 33.) The **anhydrides** (see p. 61) are derived from acids by removal of water. Thus: $2\text{HNO}_3 - \text{H}_2\text{O} = \text{N}_2\text{O}_5$; $\text{H}_2\text{SO}_4 - \text{H}_2\text{O} = \text{SO}_3$; $2\text{H}_3\text{PO}_4 - 3\text{H}_2\text{O} = \text{P}_2\text{O}_5$.

Composition and Constitution.—The characters of a compound depend not only upon the kind and number of its atoms, but also upon the manner in which they are attached to each other. There are, for instance, two substances, each having the **empirical formula** $\text{C}_2\text{H}_4\text{O}_2$, one of which is a strong acid, the other a neutral ester. As the molecule of each contains the same number and kind of atoms, the differences in their properties must be due to differences in the manner in which the atoms are linked together.

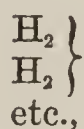
The composition of a compound is the number and kind of atoms contained in its molecule; and is shown by its empirical formula.

The constitution of a compound is the number and kind of atoms and their relations to each other, within its molecule; and is shown by its rational formula.

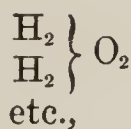
A rational formula is one which partly or completely indicates the

constitution of the body. Rational formulæ are either **typical** or **graphic**. In the system of **typical formulæ** all substances are considered as being so constituted that their rational formulæ may be referred to one of three classes or **types**, or to a combination of two of these types. These three classes, being named after the most common substance occurring in each, are expressed thus:

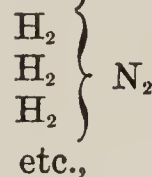
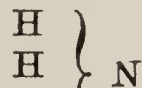
The hydrogen
type.



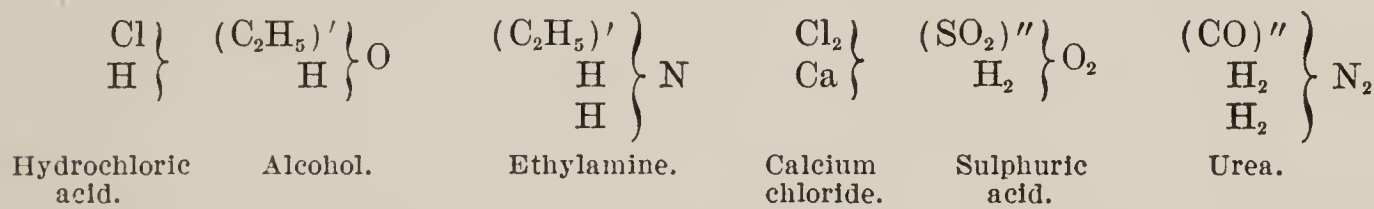
The water
type.



The ammonia
type.



it being considered that the formula of any substance of known constitution can be indicated by substituting the proper element, or radical, for one or more of the atoms of the type, thus:

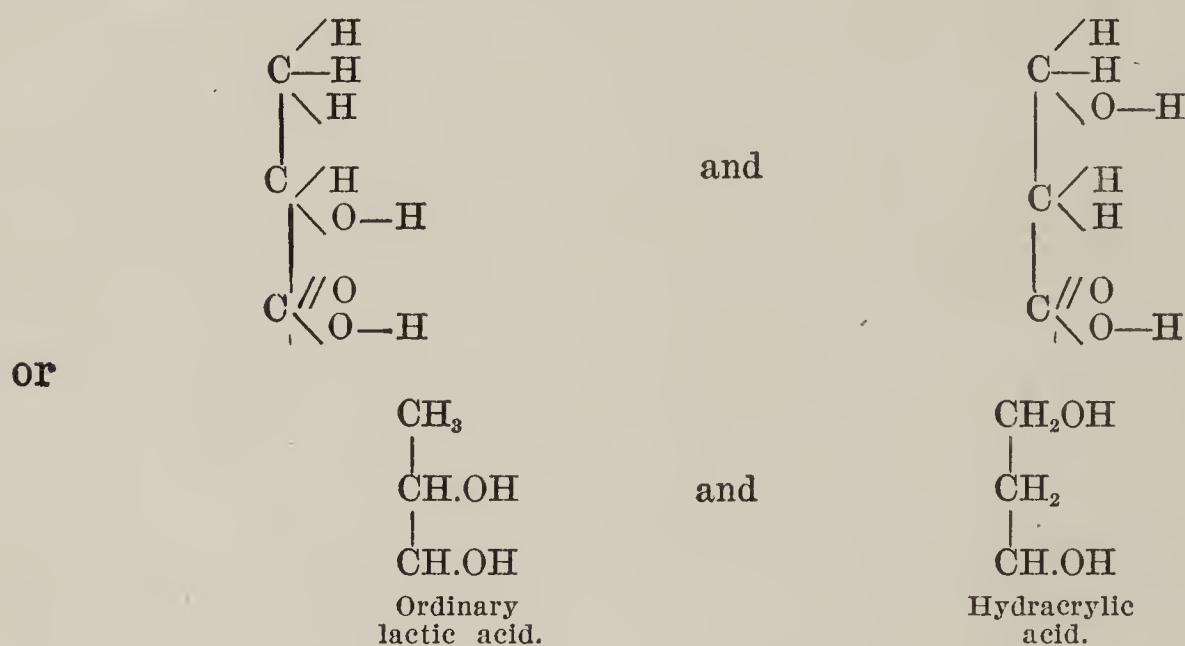


Typical formulæ are of great service in the classification of compound substances, as well as to indicate, to a certain degree, their nature and the method of the reactions into which they enter. Thus in the case of the two substances mentioned above (p. 46), as both having the composition $\text{C}_2\text{H}_4\text{O}_2$, we find on examination that one contains the group $(\text{CH}_3)'$, while the other contains the group $(\text{C}_2\text{H}_3\text{O})'$. The difference in their constitution at once becomes apparent in their typical formulæ, $\begin{array}{c} (\text{CHO})' \\ (\text{CH}_3)' \end{array} \left. \vphantom{\begin{array}{c} (\text{CHO})' \\ (\text{CH}_3)' \end{array}} \right\} \text{O}$ and $\begin{array}{c} (\text{C}_2\text{H}_3\text{O})' \\ \text{H} \end{array} \left. \vphantom{\begin{array}{c} (\text{C}_2\text{H}_3\text{O})' \\ \text{H} \end{array}} \right\} \text{O}$, indicating differences in their properties, which we find upon experiment to exist. The first substance is neutral in reaction and possesses no acid properties; it closely resembles a salt of an acid having the formula $\begin{array}{c} (\text{CHO})'' \\ \text{H} \end{array} \left. \vphantom{\begin{array}{c} (\text{CHO})'' \\ \text{H} \end{array}} \right\} \text{O}$. The second substance, on the other hand, has a strongly acid reaction, and markedly acid properties, as indicated by the oxidized radical and the extra-radical hydrogen. It is capable of forming salts by the substitution of an atom of a univalent, basylous element for its single replaceable atom of hydrogen: $\begin{array}{c} (\text{C}_2\text{H}_3\text{O})' \\ \text{Na} \end{array} \left. \vphantom{\begin{array}{c} (\text{C}_2\text{H}_3\text{O})' \\ \text{Na} \end{array}} \right\} \text{O}$.

Although typical formulæ have been and still are of great service, many cases arise, especially in treating of the more complex organic substances, in which they do not sufficiently indicate the relations between the atoms which constitute the molecule, and thus fail to convey a proper idea of the nature of the substance. Considering,

for example, the ordinary lactic acid, we find its composition to be $C_3H_5O_3$, which, expressed typically, would be $(C_3H_4O)'' \left\{ \begin{smallmatrix} H_2 \\ O_2 \end{smallmatrix} \right\}$, a constitution supported by the fact that the radical $(C_3H_4O)''$ may be obtained in other compounds, as $(C_3H_4O)'' \left\{ \begin{smallmatrix} Cl_2 \end{smallmatrix} \right\}$. This constitution, however, cannot be the true one, because, in the first place lactic acid is not dibasic, but monobasic; and in the second place, there is another acid, called hydracrylic acid, having an identical composition, yet differing in its products of decomposition. These differences in the properties of the two acids must be due to a different *arrangement* of atoms in their molecules, a view which is supported by the sources from which they are obtained and the nature of their products of decomposition.

To express the constitution of such bodies **graphic formulæ** are used, in which the position of each atom in relation to the others is set forth. The constitution of the two lactic acids would be expressed by graphic formulæ in this way:



Graphic formulæ are usually still further abbreviated, bonds being indicated by dots; thus: $CH_3.CHOH.CO_2H$, and $CH_2OH.CH_2.CO_2H$.

Chemical Energy—Affinity—Displacement—Stability.—Chemical energy, frequently spoken of as chemical affinity, chemical force, or chemism, is that form of energy by which the atoms are held together in the molecule, and by which, under suitable physical conditions, the attachments and arrangement of atoms are changed.

The atoms of different elements do not exhibit the same tendency to enter into combination with the atoms of a given element. Thus chlorine and oxygen readily combine with hydrogen, while the metals, except the alkaline metals and palladium, do not do so at all. Oxygen enters into the combination with all the other elements except fluorine and the elements of the argon group, while the last-named form no compound with any other element. Such differences in tendency to

union are referred to by saying that the elements have strong or weak **affinity**.

Frequently when an element is brought in contact with a compound the free element **displaces** one of those contained in the compound; as when chlorine is in contact with sodium iodide, sodium chloride is formed and iodine liberated: $2\text{NaI} + \text{Cl}_2 = 2\text{NaCl} + \text{I}_2$. This is ascribed to the greater affinity of chlorine.

There are also differences in the degree of permanence of compounds under the influence of slight variations in physical conditions. Thus, of the two compounds of hydrogen and oxygen, one, water, is dissociated only at very high temperatures, while the other, hydrogen dioxide, is decomposed by very slight heating. These variations are referred to by saying that certain compounds are **stable**, others **labile**, or **unstable**. The stability of the compound depends upon the affinities, the proportions, and the arrangement of the atoms in the molecule.

Chemical Equilibrium.—When two or more substances are brought together, their association constitutes a **chemical system**. In this system an action may be set up, which will proceed to a certain point, and then cease. The system is then said to be in **chemical equilibrium**. - As in mechanical, so in chemical equilibrium the condition of rest does not imply that no force is in action, but that the forces acting neutralize each other in such manner that their algebraic sum is zero; the condition is one of *dynamic* equilibrium.

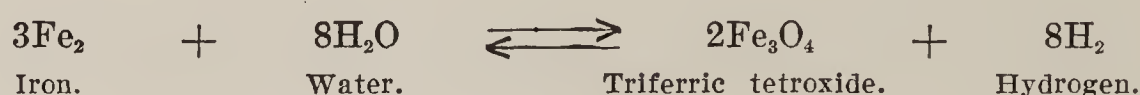
As the “physical” conditions of concentration, pressure and temperature exert great influence upon the occurrence and extent of chemical changes, these must be taken into account along with affinity; and the “physical” phenomena of solution, and changes of state of aggregation must also be considered along with changes of composition in the consideration of chemical equilibrium.

Equilibrium in a system all parts of which have the same physical properties and the same chemical composition, as in a solution or in a mixture of liquids or of gases, is distinguished as **homogeneous equilibrium**; while **heterogenous equilibrium** occurs in a system the parts of which are separated by bounding surfaces, as when solids and liquids, or immiscible liquids are in contact.

Distinction must also be made between **real** and **apparent** equilibrium. In a state of **real equilibrium** there is no change of relations, however slight or however slow, so long as the conditions of concentration, pressure and temperature remain constant, and changes which are caused by variations in these conditions take place regularly and continuously. Thus, in a system composed of a solution in contact with excess of the solute, variations in the proportions of the solute in the solution take place regularly with variations of temperature. Moreover, in this case the same condition of equilibrium is

reached, whether it is approached from one side or from the other. Thus, a solution at a given temperature contains the same proportion of solute, whether it is obtained by addition to an unsaturated solution, or by deposition from a supersaturated solution. In a condition of **apparent equilibrium** it is probable that change is continuously taking place, although frequently with such extreme slowness that it escapes observation, even at constant concentration, temperature and pressure. Such changes as are caused by variations in these conditions in apparent equilibrium may, within certain limits, occur with regularity, but beyond these limits a sudden and more or less violent change takes place, after which the relations which existed previously are not restored by a return to the original conditions. Thus, in a system consisting of water and a mixture of hydrogen and oxygen, with moderate variation of temperature and pressure there are slight and regular variations in the amount of oxygen dissolved in the water, but at a certain elevation of temperature a sudden combination of the gases to form water takes place and, on cooling, the gases do not reappear.

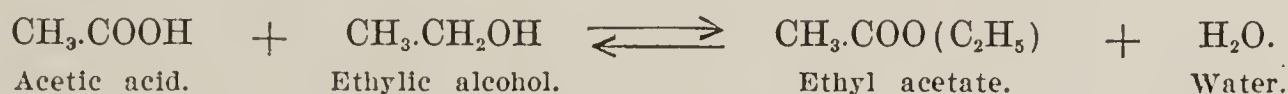
Reversible Reactions.—Many reactions are known to occur in which displacements may be brought about in opposite directions. Clearly in these some influence other than affinity must determine in which direction the reaction will occur. Such are called **reversible reactions**, or **reversed actions**. Thus, if iron is heated in an atmosphere of vapor of water, the iron displaces the hydrogen of the water, which is liberated, and combines with the oxygen to form oxide of iron. If, on the other hand, oxide of iron is heated in an atmosphere of hydrogen, the hydrogen displaces the iron, which is liberated, and combines with the oxygen to form water. The reaction may take place, therefore, according to the following equation, read either from left to right, or from right to left:



If we start with pure iron and vapor of water the reaction will proceed according to the equation read from left to right until the proportion of hydrogen and water vapor present has reached a certain ratio, when the action will cease, and the system will be in equilibrium. Starting with pure oxide of iron and hydrogen, on the other hand, the reaction will proceed according to the equation read from right to left, and will cease when the ratio of hydrogen to water vapor will have acquired the same value as that reached in the first instance. As the condition of equilibrium reached in the two cases is the same when produced by proceeding in either direction, it is one of real equilibrium, and, as might be expected, if a mixture of iron and oxide of iron be heated in an atmosphere composed of hydrogen and

water vapor in the proportion reached in either of the two former reactions, no change whatever will occur.

Mass Action.—The example of a reversible reaction given above was one in a *heterogeneous system*, composed of solids and gases. As an example of a reaction of this kind occurring in a *homogeneous system*, a solution, we may consider that represented by the following equation:



If we start with ethyl alcohol and acetic acid, the reaction will proceed according to the equation, read from left to right; but if we start with ethyl acetate and water it will proceed from right to left. In neither case, however, will it be complete. If one mol each of the reacting substances have been used, real equilibrium will have been established and the reaction will have ceased when the composition of the mixture has become: $\frac{1}{3}$ mol acetic acid, $\frac{1}{3}$ mol alcohol, $\frac{2}{3}$ mol ethyl acetate and $\frac{2}{3}$ mol water. This statement is not to be taken as meaning that when this relation is attained no further action occurs, but that the changes in one direction have become equal in unit time to those in the opposite direction; the equilibrium being dynamic, not static.

Chemical effects of light.—Many chemical combinations and decompositions are much modified by the intensity, and the kind of light to which the reacting substances are exposed. Hydrogen and chlorine gases do not combine, at the ordinary temperature, in the absence of light; in diffused daylight or gaslight, they unite slowly and quietly; in direct sunlight, or in the electric light, they unite suddenly and explosively. The salts of silver, used in photography, are not decomposed in the dark, but are rapidly decomposed in the presence of organic matter, when exposed to sunlight.

Classification of the Elements.—The elements were formerly divided into two great classes, **metals** and **metalloids**. The **metals**, being such substances as are opaque, possess what is known as metallic luster, are good conductors of heat and electricity, and are electropositive; the **metalloids**, on the other hand, such as are gaseous, or, if solid, do not possess metallic luster, have a comparatively low power of conducting heat and electricity, and are electro-negative.

This division, based upon purely physical properties, which, in many cases, are ill-defined, has become insufficient. Several elements formerly classed under the above rules with the metals, resemble the metalloids in their chemical characters much more closely than they do any of the metals. Indeed, by the characters mentioned above, it is impossible to draw any line of demarcation which shall separate the elements distinctly into two groups.

The classification of the elements should be such that each group shall contain elements whose *chemical* properties are similar—the *physical* properties being considered only in so far as they are intimately connected with the chemical. The arrangement of elements into groups is not equally easy in all cases. Some groups, as the chlorine group, are sharply defined, while the members of others differ from each other more widely in their properties. The position of most of the more recently discovered elements is still uncertain, owing to the imperfect state of our knowledge of their properties.

In this book the elements are classified according to resemblances in their *chemical properties*, based upon the nature of the oxides and the existence or non-existence of oxysalts:

Class I. Typical Elements.

Hydrogen. Oxygen.

Although these two elements differ notably in their properties, they are here classed as *typical elements*, because together they form the basis of our classification; they both play important parts in the formation of acids; neither would find a suitable place elsewhere in the classification; and they may also be considered as typical from the point of view of ionization, as they form the characterizing ions of acids and bases, hydrion and hydroxidion.

Class II. Elements which form no compounds.

Helium, neon, argon, krypton, xenon, niton.

Class III. Acidulous Elements.

Elements whose oxides unite with water to form acids, never to form bases. Which do not form oxysalts.

GROUP I.—Fluorine, chlorine, bromine, iodine.

GROUP II.—Sulphur, selenium, tellurium.

GROUP III.—Nitrogen, phosphorus, arsenic, antimony.

GROUP IV.—Boron.

GROUP V.—Carbon, silicon.

GROUP VI.—Vanadium, columbium, tantalum.

GROUP VII.—Molybdenum, tungsten, osmium.

Elements of this class are also called **non-metals**, in contradistinction to those of classes IV and V, which are collectively called **metals**. They are also referred to as **electronegative elements**, because they are electronegative to hydrogen, although they are all

electropositive to oxygen, and individual members are also electropositive to others of the class (p. 34). On electrolysis of compounds containing acidulous elements or oxygen, and metals or hydrogen, the former are usually found in the anion, the latter in the cation, as $H \cdot K \cdot | SO_4$ ". But this is not invariably the case.

Class IV. Amphoteric Elements.

Elements whose oxides unite with water, some to form bases, others to form acids. Which form oxysalts.

- GROUP I.—Gold.
- GROUP II.—Chromium, manganese, iron.
- GROUP III.—Uranium, radium, thorium.
- GROUP IV.—Lead.
- GROUP V.—Bismuth.
- GROUP VI.—Titanium, germanium, zirconium, tin.
- GROUP VII.—Palladium, platinum.
- GROUP VIII.—Rhodium, ruthenium, iridium.

The amphoteric and basylous elements are the **metals** or **electropositive elements**, and have these properties in common: they form oxysalts, and are separated as cations on electrolysis of such salts.

Class V. Basylous Elements.

Elements whose oxides unite with water to form bases, never to form acids. Which form oxysalts.

- GROUP I.—Lithium, sodium, potassium, rubidium, cæsium, silver.
- GROUP II.—Thallium.
- GROUP III.—Calcium, strontium, barium.
- GROUP IV.—Magnesium, zinc, cadmium.
- GROUP V.—Glucinum, aluminium, scandium, gallium, indium.
- GROUP VI.—Nickel, cobalt.
- GROUP VII.—Copper, mercury.
- GROUP VIII.—Yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, thulium, ytterbium.

This class includes the more strongly electropositive metals.

In classes III, IV and V the elements are subdivided into groups, the members of which have common distinctive characters, and are more or less closely allied to each other. In classes III and V the resemblances between individuals of groups occurring first in the list

TABLE TO ILLUSTRATE THE PERIODIC SYSTEM.

Series	ZERO GROUP	GROUP I — R ₂ O	GROUP II — RO	GROUP III — R ₂ O ₃	GROUP IV RH ₄ RO ₂	GROUP V RH ₃ R ₂ O ₅	GROUP VI RH ₂ RO ₃	GROUP VII RH R ₂ O ₇	GROUP VIII — RO ₄ ?
1	—	H=1	—	—	—	—	—	—	—
2	He=4	Li=7	Gl=9	B=11	C=12	N=14	O=16	F=19	—
3	Ne=20	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35.5	—
4	A=40	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Ni=58 Co=59
5	—	Cu=63	Zn=65	Ga=70	Ge=72	As=75	Se=79	Br=80	—
6	Kr=83	Rb=85	Sr=87	Yt=89	Zr=90	Cb=93	Mo=96	—	Ru=101 Rh=103 Pd=106
7	—	Ag=108	Cd=112	In=114	Sn=119	Sb=120	Te=127	I=127	—
8	Xe=130	Cs=133	Ba=137	La=139	Ce=140	Nd=144	Tb=159	—	—
9	—	—	—	—	—	Er=167	—	—	—
10	—	—	—	Yb=173	—	Ta=181	W=184	—	Os=191 Ir=193 Pt=195
11	—	Au=197	Hg=200	Tl=204	Pb=207	Bi=208	—	—	—
12	Nt=222	—	Ra=226	—	Th=232	—	U=238	—	—

The figures used as atomic weights are approximate.

For table of International Atomic Weights (1918), see page 27.

are the most marked, and are more close than those between members of groups placed lower down.

Periodic Law.—If the elements are arranged in a continuous series in the numerical order of their atomic weights: H, He, Li, Gl, *etc.*, it will be found that elements having similar properties, in themselves and in their compounds, will fall in the same (vertical) line, or group. (See table on p. 54.) This connection between the periodicity of the atomic weights of the elements and their chemical relationships is expressed in the **Periodic law** of Mendelejeff. **The properties of elements, the constitution of their compounds, and the properties of the latter are periodic functions of the atomic weights of the elements.** But the law is not absolute, and, apart from the necessity of a few transpositions, the separation into different groups of such closely related elements as Cu and Hg, Cr and Mn and Fe, and the grouping together of such dissimilar elements as Cu, Ag and Au are not in accordance with observed fact.

It will be observed that the series is complete, with but a single break, between H=1 and Tb=159, but that below that point the breaks are numerous. When the earlier tables were constructed (about 1870) the breaks were more numerous, but have been in part filled by the discovery of then unknown elements, such as scandium, gallium, germanium, and the entire argon group. It may, therefore, be expected that other breaks, still existing, may be filled by the discovery of other new elements of very high or very low atomic weights.

INORGANIC CHEMISTRY

CLASS I.—TYPICAL ELEMENTS.

HYDROGEN—OXYGEN.

ALTHOUGH, in a strict sense, hydrogen is regarded by most chemists as the one and only type-element—that whose atom is the unit of atomic and molecular weights—the important part which oxygen plays in the formation of those compounds whose nature forms the basis of our classification, its acid-forming power in organic compounds, and the differences existing between its properties and those of the elements of the sulphur group, with which it is usually classed, warrant us in separating it from the other elements and elevating it to the position it here occupies.

HYDROGEN.

Symbol = H—Univalent—Atomic weight = 1 (International = 1.008)—Molecular weight = 2—Sp. gr. = 0.06926A—One litre weighs 0.0899 gram—1 gram measures 11.16 litres.

Occurrence.—Occurs *free* in volcanic gases, in fire-damp, occluded in meteorites, in the gases exhaled from the lungs, and in those of the stomach and intestine. *In combination* in water, acids, hydrogen sulphide, ammoniacal compounds, and in many organic substances.

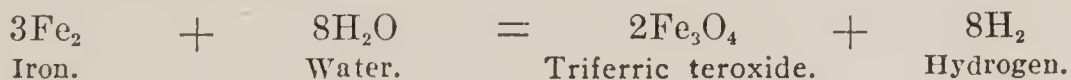
Preparation.—(1) By electrolysis of acidulated water, H is given off at the negative pole. Utilized when pure H is required.

(2) By the dissociation of water at very high temperatures.

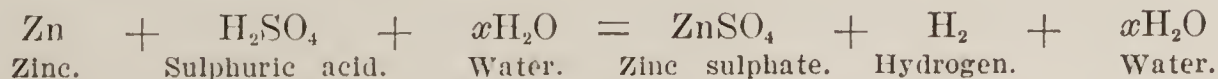
(3) By the decomposition of water by certain metals. The alkali metals decompose water at the ordinary temperature:



Some other metals, such as iron and copper, effect the decomposition only at high temperatures:



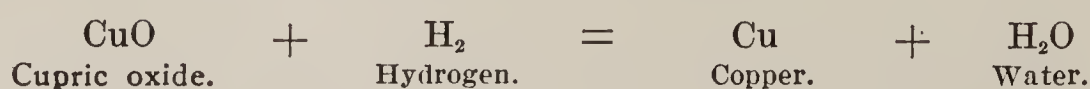
(4) By decomposition of mineral acids, in the presence of water, by zinc and certain other metals:



Properties.—*Physical.*—Hydrogen is a colorless, odorless, tasteless gas; 14.47 times lighter than air, being the lightest substance known. The weight of a litre, 0.0896 gram, is called a *crith*. It is almost insoluble in water and alcohol. It conducts heat and electricity better than any other gas. In obedience to **Graham's law**: **The diffusibility of two gases varies inversely as the square roots of their densities**, it is the most rapidly diffusible of gases. The rapidity with which this diffusion takes place renders the use of hydrogen, which has been kept for even a short time in gas bags or gasometers, dangerous. It is liquefied at -240° under a pressure of 13.3 atm. The liquid is clear and colorless, boils at -253° , only 20° above the absolute zero, and has a sp. gr. of 0.068.

Certain metals have the power of absorbing large quantities of hydrogen, which is then said to be **occluded**, and this action of the metal is called **occlusion**. Palladium absorbs 980 volumes of the gas when used as the negative electrode in the electrolysis of water. The occluded gas is driven off by the application of heat, and possesses great chemical activity, similar to that which it has when in the nascent state. This latter quality, and the fact that heat is liberated during the occlusion, would seem to indicate that the gas is contained in the metal, not in a mere physical state of condensation, but in chemical combination.

Chemical.—Hydrogen exhibits no great tendency to combine with other elements at ordinary temperatures. It combines explosively, however, with chlorine under the influence of sunlight, and with fluorine even in the dark. It does not support combustion, but, when ignited, burns with a pale blue and very hot flame; the result of the combination being water. Mixtures of hydrogen and oxygen explode violently on the approach of flame, or by the passage of the electric spark, the explosion being caused by the sudden expansion of the vapor of water formed, under the influence of the heat of the reaction. In a mixture of hydrogen and oxygen at the ordinary temperature formation of water takes place with extreme slowness. If a piece of platinum foil is introduced into the mixture combination occurs with sensible rapidity, and, if the platinum is finely divided, the rapidity of the combination is such that the metal becomes incandescent, and explodes the mixture. The platinum here is said to be a **catalyser**, *i.e.*, a substance by whose presence the velocity of a reaction is accelerated. Catalysers are also called **contact agents**. Many compounds containing oxygen give up that element when heated in an atmosphere of hydrogen:



The removal of oxygen from a compound is called a **reduction** or **deoxidation**. In a broader sense the term reduction is applied to

any diminution in the relative quantity of the electronegative factor in a compound. Thus mercuric chloride, HgCl_2 (Hg 200: Cl 71) is *reduced* to mercurous chloride HgCl (Hg 200: Cl 35.5).

At the instant that H is liberated from its compounds it has a deoxidizing power similar to that which ordinary H possesses only at elevated temperatures, and its tendency to combine with other elements is greater than under other conditions. The greater energy of H, and of other elements as well, in this **nascent state**, may be thus explained. Free H exists in the form of molecules, each one of which is composed of two atoms, but at the instant of its liberation from a compound, it is in the form of individual atoms, and that portion of force required to split up the molecule into atoms, necessary when free H enters into reaction, is not required when the gas is in the nascent state.

In its physical and chemical properties, hydrogen more closely resembles those usually ranked as metals than it does those forming the class of non-metals, among which it is usually placed. Its conducting power, as well as its relation to the acids, which may be considered as salts of H, tend to separate it from the non-metals.

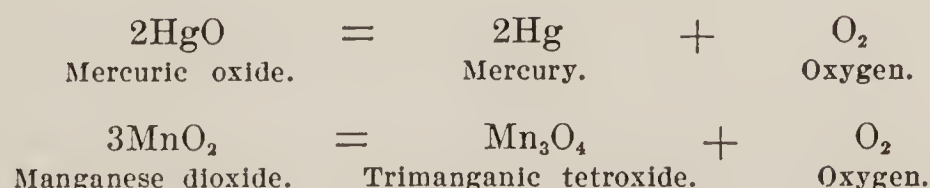
Analytical Characters.—(1) Burns with a faintly blue flame, which deposits water on a cold surface brought over it; (2) Mixed with oxygen, explodes on contact with flame, producing water.

OXYGEN.

Oxygenium (U. S. P.) *Symbol*=O—*Bivalent*—*Atomic weight*=16; *molecular weight*=32.—*Sp. gr.*=1.10563 A (*calculated*=1.1088); 15.95 H.

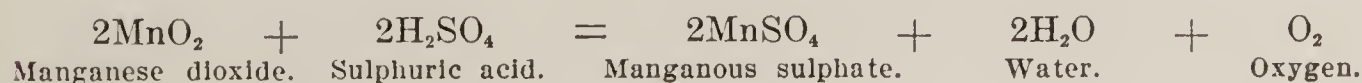
Occurrence.—Oxygen is the most abundant of the elements. It exists *free* in atmospheric air; *in combination* in a great number of substances, mineral, vegetable, and animal; it occurs in rocks and minerals (about 30 to 50 per cent. of the earth's crust), in water it is eight-ninths by weight.

Preparation.—(1) By heating certain oxides:

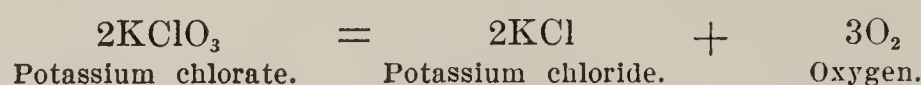


(2) By the electrolysis of water, acidulated with sulphuric acid, O is given off at the positive pole.

(3) By the action of sulphuric acid upon certain compounds rich in O: manganese dioxide, potassium dichromate, and plumbic peroxide:



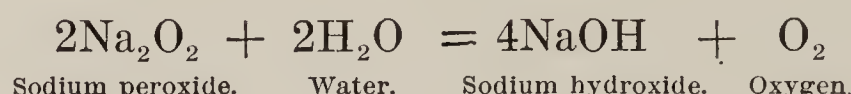
(4) The best method, and that usually adopted, is by heating a mixture of potassium chlorate and manganese dioxide in equal parts. The chlorate gives up all its O, according to the equation:



A small quantity of free chlorine usually exists in the gas produced by this reaction. If the oxygen is to be used for inhalation, the chlorine should be removed by allowing the gas to stand over water for 24 hours.

(5) By the decomposition by heat of certain salts rich in O: alkaline permanganates, nitrates and chlorates.

(6) By the action of water upon sodium peroxide:



Oxygen is official in the U. S. P. as *Oxygenium*; it contains not less than 95 per cent. by volume of O, and for convenience it is usually compressed in metal cylinders.

Properties.—*Physical.*—Oxygen is a colorless, odorless, tasteless gas, soluble in water in the proportion of 7.08 cc. in 1 litre of water at 14.8°, somewhat more soluble in absolute alcohol. It liquefies at −140° under a pressure of 300 atmospheres. Liquid oxygen boils at −187.4° at the ordinary pressure.

Chemical.—Oxygen is characterized, chemically, by the strong tendency which it exhibits to enter into combination with other elements. It forms binary compounds with all elements except fluorine and bromine. With most elements it unites directly, especially at elevated temperatures. In many instances this union is attended by the appearance of light, and always by the extrication of heat. The luminous union of O with another element constitutes the familiar phenomenon of **combustion**, and is the principal source from which we obtain so-called artificial heat and light. A body is said to be **combustible** when it is capable of so energetically combining with the oxygen of the air as to liberate light as well as heat. Gases are said to be **supporters of combustion**, when combustible substances will unite with them, or with some of their constituents, the union being attended with the appearance of heat and light. The distinction between combustible substances and supporters of combustion is, however, one of mere convenience. The action taking place between the two substances, one is as much a party to it as the other. A jet of air burns in an atmosphere of coal-gas as readily as a jet of coal-gas burns in air.

An **oxidation** is a chemical action in which oxygen combines with an element or a compound. The burning of coal: $\text{C} + \text{O} = \text{CO}$ or $\text{C} + \text{O}_2 = \text{CO}_2$; and the formation of acetic acid from alcohol:

$C_2H_6 + O_2 = C_2H_4O_2 + H_2O$, are oxidations. In a broader sense the word "oxidation" is sometimes used as the opposite to "reduction" (p. 58) to apply to any increase in the relative quantity of the electro-negative element in a compound. Thus the conversion of $FeCl_2$ (Fe 56:Cl 71) into $FeCl_3$ (Fe 56:Cl 106.5) may be referred to as an oxidation, although it is, more properly, a chlorination.

The compounds of oxygen—the **oxides**—are divisible into three groups:

1. **Anhydrides**.—Oxides capable of combining with water to form *acids*. Thus *sulphuric anhydride*, SO_3 , unites with water to form *sulphuric acid*, H_2SO_4 .

The term anhydride is not limited in application to *binary* compounds, but applies to *any substance capable of combining with water to form an acid*. Thus the compound $C_4H_6O_3$ is known as acetic anhydride, because it combines with water to form acetic acid: $C_4H_6O_3 + H_2O = 2C_2H_4O_2$. (See compounds of arsenic and sulphur.)

2. **Basic oxides** are such as combine with water to form bases. Thus calcium oxide, CaO , unites with water to form calcium hydroxide, CaH_2O_2 .

3. **Saline, neutral or indifferent oxides** are such as are neither acid nor basic in character. In some instances they are essentially neutral, as in the case of hydrogen monoxide, or water. In other cases they are formed by the union of two other oxides, one basic, the other acid in quality, such as the red oxide of lead, Pb_3O_4 , formed by the union of a molecule of the acidulous peroxide, PbO_2 , with two of the basic protoxide, PbO . It is to oxides of this character that the term "saline" properly applies.

The process of *respiration* is very similar to combustion, and as oxygen gas is the best supporter of combustion, so, in the diluted form in which it exists in atmospheric air, it is not only the best, but the only supporter of animal respiration. (See Carbon dioxide.)

Analytical Characters.—1. A glowing match-stick bursts into flame in free oxygen. 2. Free O, when mixed with nitrogen dioxide, produces a brown gas.

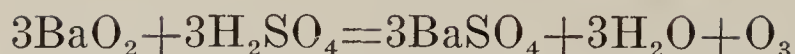
OZONE.

Allotropic oxygen (see Allotropy, p. 9).—*Formula* $= O_3$. *Molecular weight* $= 48$.—Air through which discharges of static electricity have been passed, and oxygen obtained by the decomposition of water (if electrodes of gold or platinum be used), have a peculiar odor, somewhat resembling that of sulphur, which is due to the conversion of a part of the oxygen into ozone.

Preparation.—(1) By the decomposition of water by the battery.

(2) By the slow oxidation of phosphorus in damp air.

(3) By the action of concentrated sulphuric acid upon barium dioxide:



(4) By the passage of silent electric discharges through air or oxygen.

Properties.—When pure, it is a dark liquid, almost opaque in layers 2 mm. thick, which is not decomposed at the ordinary temperature, but converted into a bluish gas. It boils at -119° .

When oxygen is ozonized it contracts slightly in volume, and when the ozone is removed from ozonized oxygen by mercury or potassium iodide the volume of the gas is not diminished. These facts, and the great chemical activity of ozone, have led chemists to regard it as condensed oxygen; the molecule of ozone being represented thus (OOO), while that of ordinary oxygen is (OO): $3\text{O}_2 = 2\text{O}_3$.

Ozone is very sparingly soluble in water, more soluble in the presence of hypophosphites, insoluble in solutions of acids and alkalies. In the presence of moisture it is slowly converted into oxygen at 100° , a change which takes place rapidly and completely at 237° . It is a powerful oxidant; it decomposes solutions of potassium iodide with formation of potassium hydroxide, and liberation of iodine; it oxidizes all metals except gold and platinum, in the presence of moisture; it decolorizes indigo and other organic pigments, and acts rapidly upon rubber, cork, and other organic substances.

Analytical Characters.—(1) Neutral litmus paper, impregnated with solution of potassium iodide, is turned blue when exposed to air containing ozone. The same litmus paper without iodide is not affected. (2) Manganous sulphate solution is turned brown by ozone. (3) Solutions of thallous salts are colored yellow or brown by ozone. (4) Paper impregnated with fresh tincture of natural (unpurified) guaiacum is colored blue by ozone. (5) Metallic silver is blackened by ozone.

When inhaled, air containing 0.07 gram of ozone per litre causes intense coryza and hemoptysis. It is probable that ozone is by no means as constant a constituent of the atmosphere as was formerly supposed. (See Hydrogen dioxide.)

COMPOUNDS OF HYDROGEN AND OXYGEN.

Two are known—hydrogen monoxide or water, H_2O ; hydrogen dioxide or oxygenated water, H_2O_2 .

WATER.

H_2O —*Molecular weight*=18—*Sp. gr.*=1—*Vapor density*=0.6218
A; *calculated*=0.6234.

Occurrence.—In unorganized nature H_2O exists in the gaseous

form in atmospheric air and in volcanic gases; in the liquid form very abundantly; and as a solid in snow, ice, and hail.

As water of crystallization it exists in definite proportions in certain crystals, to the maintenance of whose shape it is necessary.

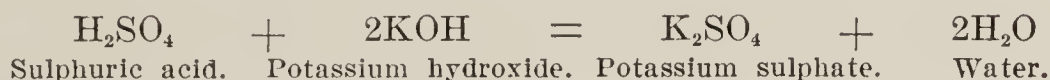
In the organized world H_2O forms a constituent part of every tissue and fluid.

Formation.—Water is formed: (1) By union, brought about by elevation of temperature, of one vol. O with two vols. H.

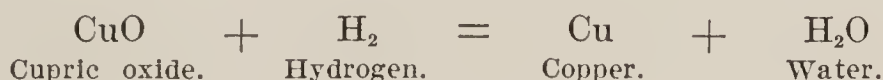
(2) By burning H, or substances containing it, in air or in O.

(3) By heating organic substances containing H to redness with cupric oxide, or with other substances capable of yielding O. This method of formation is utilized to determine the amount of H contained in organic substances.

(4) When an acid and a hydroxide react upon each other to form a salt:



(5) When a metallic oxide is reduced by hydrogen:



(6) In the reduction and oxidation of many organic substances.

Pure H_2O is not found in nature. When required free from ordinary impurities it is separated from suspended matters by filtration, and from dissolved substances by distillation.

Properties.—*Physical.*—With a barometric pressure of 760 mm. H_2O is solid below 0° ; liquid between 0° and 100° ; and gaseous above 100° .

Water is the best solvent we have, and acts in some instances as a simple solvent, in others as a chemical solvent.

Vapor of water is colorless, transparent, and invisible. The latent heat of vaporization of water is 536.5; that is, as much heat is required to vaporize 1 kilo. of water at 100° as would suffice to raise 536.5 kilos. of water 1° in temperature. In passing from the liquid to the gaseous state, water expands 1,696 times in volume.

Chemical.—Water may be shown to consist of 1 vol. O and 2 vols. H, or 8 by weight of O and 1 by weight of H, either by analysis or synthesis.

Analysis is the reducing of a compound to its constituent parts or elements.

Synthesis is the formation of a compound from its elements. A partial synthesis is one in which a complex compound is produced from a simpler one, but not from the elements.

Water may be resolved into its constituent gases: (1) By elec-

trolysis of acidulated water; H being given off at the negative and O at the positive pole.

(2) By passing vapor of H_2O through a platinum tube heated to whiteness, or through a porcelain tube heated to about $1,100^\circ$. The decomposition of a compound gas or vapor by elevation of temperature is called **dissociation**.

(3) By the action of the alkali metals. Hydrogen is given off, and the metallic hydroxide remains in solution in an excess of H_2O .

(4) By passing vapor of H_2O over red-hot iron. Oxide of iron remains and H is given off.

Water combines with oxides to form new compounds, some of which are acids and others bases, known as **hydroxides**.

A hydroxide is a compound formed by the replacement of half of the hydrogen of water by another element or by a radical.

A hydrate is a compound containing chemically combined water. The act of union of a substance with water is referred to as **hydration**.

The hydroxides of the electro-negative elements and radicals are **acids**; most of those of the electro-positive elements and radicals are **basic hydroxides**.

Certain substances, in crystallizing, combine with a definite proportion of water, which is known as **water of crystallization**, and whose presence, although necessary to the maintenance of certain physical characters, such as color and crystalline form, does not modify their chemical reactions. In many instances a portion of the water of crystallization may be driven off at a comparatively low temperature, while a higher temperature is required to expel the remainder. This latter is known as **water of constitution**.

The symbol Aq (Latin, *aqua*) is frequently used to designate the water of crystallization, the water of constitution being indicated by H_2O . Thus $\text{MgSO}_4 \cdot \text{H}_2\text{O} + 6\text{Aq}$ represents magnesium sulphate with one molecule of water of constitution and six molecules of water of crystallization. We consider it preferable, however, as the distinction between water of crystallization and water of constitution in many salts is only one of degree and not of kind, to use the symbol Aq to designate the sum of the two; thus, $\text{MgSO}_4 + 7\text{Aq}$.

Water decomposes the chlorides of the third class (see p. 52) of elements (those of carbon only at high temperatures and under pressure). Thus phosphorous trichloride forms phosphorous and hydrochloric acids: $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCl}$. A decomposition attended with absorption of water is called **hydrolysis**.

Natural Waters.—Natural waters which appear to the senses to be fit for drinking are called **potable waters**, in contradistinction to such as are, from their taste and appearance, obviously unfit for that use.

Potable waters may be classified, according to their origin, into four groups:

(1) **Meteoric waters:** rain water and melted snow. These are the purest

natural waters if uncontaminated; they contain very small quantities of solids, and are highly aerated. Rain water falling during the first part of a shower is less pure than that which falls subsequently. In districts where notable quantities of coal which contain sulphur are burnt, rain water contains more sulphates, ammoniacal salts, nitrates and nitrites than elsewhere.

(2) **Surface waters:** the waters of rivers, lakes and ponds. These are mixtures, in varying proportions, of rain water, spring water and the drainage of the surrounding land. They vary greatly in natural purity, and are frequently contaminated by sewage and other refuse.

(3) **Ground waters:** water which permeates the superficial stratum above the uppermost impermeable rock. This is the water obtained in surface wells and in driven wells. Its quality depends upon what is in and on the stratum in which the well is dug; a driven well in a sandy stratum remote from habitations yields an excellent water, while the water of a well near a privy vault or a defective sewer is more or less diluted sewage. In limestone districts ground water is hard.

(4) **Deep waters:** spring waters and those of artesian wells.

Spring water is rain water which, having percolated through a portion of the earth's crust (in which it may also have been subjected to pressure), has become charged with solid and gaseous matter, varying in kind and quantity according to the nature of the strata through which it has percolated, the duration of contact, and the pressure to which it was subject during such contact.

Spring waters from igneous rocks and from the older sedimentary formations are fresh and sweet, and any spring water may be considered such whose temperature is less than 20° , and which does not contain more than 40 parts in 100,000 of solid matter; provided that a large proportion of the solid matter does not consist of salts having a medicinal action, and that sulphurous gases and sulphides are absent.

Artesian wells are artificial springs, produced by boring in a low-lying district, until a pervious layer, between two impervious strata, is reached; the outcrop of the system being in an adjacent elevated region.

Properties of Potable Waters.—A water to be fit for drinking purposes should be cool, limpid and odorless; it should have an agreeable taste, neither flat, salty, nor sweetish, and it should dissolve soap readily, without formation of any flocculent precipitate. But, while it is safe to condemn a water which does not possess the above characters, it is by no means safe to regard all waters which do possess them as beyond suspicion.

Impurities.—The most dangerous of all contaminations of drinking waters is by admixture of sewage, which may be present in a water in quantity sufficient to render it unfit for use and the water yet retain all of the characters of a good water above referred to. To determine whether a water is really fit for drinking a chemical analysis and a bacteriological examination are necessary. For both of these methods the student is referred to treatises on that subject. The constituents usually determined, and the interpretation of the results, are as follows:

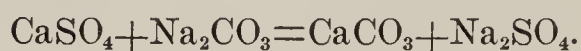
Total Solids.—The amount of solid material dissolved in potable waters varies from 4.3 to 50 in 100,000 (2.5 to 29.2 grains per U. S. gal.); and a water containing more than the latter quantity is to be condemned on that account alone.

Chlorides.—The presence of the chlorides of the alkaline metals, in quantities not sufficient to be detectable by the taste, is of no importance *per se*; but in connection with the presence of organic impurity, a determination of the amount of chlorine affords a ready method of indicating the probable source of the organic contamination. As vegetable organic matter brings with it but small quantities of chlorides, while animal contaminations are rich in those compounds, the presence of a large amount of chlorine serves to indicate that

organic impurity is of animal origin. Indeed, when time presses, as during an epidemic, it is best to rely upon determinations of chlorine, and condemn all waters containing more than 1.7 in 100,000 (1 grain per U. S. gal.) of that element.

Hardness.—The greater part of the solid matter dissolved in natural fresh waters consists of the salts of calcium, accompanied by less quantities of the salts of magnesium. The calcium salt is usually the bicarbonate or the sulphate; sometimes the chloride, phosphate, or nitrate.

A water containing an excess of calcareous salt is said to be **hard**, and one not so charged is said to be **soft**. If the hardness is due to the presence of the bicarbonate it is **temporary**, if due to the sulphate it is **permanent**. Calcium carbonate is almost insoluble in pure water, but in the presence of free carbonic acid the more soluble bicarbonate is dissolved. But, on the water being boiled, it is decomposed, with precipitation of the carbonate. As calcium sulphate is held in solution by virtue of its own, albeit sparing, solubility, it is not deposited when the water is boiled; the addition of sodium carbonate permanently softens hard water:



Rain water is the softest water.

The hardness is now usually reported in terms of calcium carbonate, CaCO_3 , either in grains per gallon or parts in 100,000. It is also sometimes reported in "degrees," which represent grains of CaCO_3 per imperial gallon. Very soft waters contain about 5CaCO_3 in 100,000, and hard waters 15 or over. Usually a water containing more than 20CaCO_3 in 100,000 is considered too hard for domestic use, unless softened by boiling. But a water is not to be condemned solely because its hardness exceeds this limit, because in certain limestone districts all waters are very hard.

Waters which owe their hardness to excess of magnesium salts, cause intestinal disturbances in those not habituated to them.

Organic Matter.—Technically, organic impurities in a water consist of vegetable or animal matters containing nitrogen. We have seen that the quantity of chlorine affords an indication as to whether the organic impurity found to be present is of vegetable or of animal origin. Animal organic contamination has its origin in sewage, and its presence consequently indicates that the water is, or may at any moment become, the means of transmitting water-borne diseases, such as typhoid and cholera.

The nitrogenous substances in feces and urine consist of albuminous bodies, crystalline organic compounds (such as urea, leucin, etc.) and ammoniacal salts. By the action of micro-organisms, which exist in the soil and in water, the albuminous and crystalline compounds are gradually converted into ammonium compounds, which are subsequently oxidized by atmospheric or dissolved oxygen, aided by bacterial influence, to nitrites and later to nitrates. Consequently the amount of sewage contamination, and the degree in which such contamination has been subsequently modified, can be inferred from quantitative determinations of the nitrogen present in the several forms referred to.

In the usual process of water analysis the following factors are determined quantitatively:

A. Albuminoid ammonia, which represents the nitrogen present in albuminous and crystalline combination.

B. Free ammonia, which represents the ammoniacal compounds.

C. Nitrogen in nitrates and nitrites.

D. Nitrites.

If a water yields no **albuminoid ammonia** it is organically pure, even if it contains much free ammonia and chlorides. If it contains from .02 to .05 milligrams per litre (.002 to .005 in 100,000) it is still quite pure. When the

albuminoid ammonia reaches 0.1 milligr. per litre (.01 in 100,000) the water is to be looked upon with suspicion; and it is to be condemned when the proportion reaches 0.15 (.015 in 100,000).

When **free ammonia** is also present in considerable quantity, a water yielding 0.05 (.005 in 100,000) of albuminoid ammonia is to be looked upon with suspicion.

Nitrates and nitrites are present in rain water in quantities less than 0.5 in 100,000, calculated as nitrogen. When the amount exceeds this, these salts are considered as indicating previous contamination by organic matter which has been oxidized and whose nitrogen has been to some extent converted into nitrites and nitrates.

The quantity of nitrites in good waters does not exceed .002 in 100,000 when they are present. A larger quantity is considered as indicating previous organic contamination.

Poisonous Metals.—Natural waters containing notable quantities of iron compounds belong to the class of chalybeate mineral waters. Contact with metallic iron does not contaminate water. In districts where copper deposits exist the waters sometimes contain copper, and the waters of some streams contain arsenic.

Lead in drinking water has been a prolific source of chronic lead poisoning. As lead is only dissolved by water after oxidation, conditions favoring oxidation of the metal favor its solution. Such conditions are: the presence of nitrates, a highly aerated condition of the water, alternate wetting and drying of the surface of the metal, the absence of sulphates and carbonates, and the presence of much carbonic acid dissolved under pressure (soda water). Sulphates and carbonates prevent solution by the formation of a protecting coating of an insoluble salt. As a rule, the purer the water the more liable it is to dissolve lead when brought in contact with that metal, especially if the contact occurs when the water is at a high temperature, or when it lasts for a long period.

Purification of Water.—The artificial means of rendering a more or less contaminated water fit for use are of five kinds: Distillation, subsidence, filtration, precipitation, and boiling.

Distillation is resorted to in the laboratory to obtain very pure water, also, on a larger scale, to purify drinking water. When water is distilled, the first portion should not be used, because it contains the gaseous impurities; and the last part should not be used, because it contains the solid impurities. Distilled water is official in the U. S. P. as *Aqua destillata*. When distilled water is to be used for drinking it should be aerated and charged with salts to the extent of about 0.03 gram each of calcium bicarbonate and sodium chloride to the litre.

In **filtration** suspended impurities are removed more or less completely by passing the water through a porous material. In *filter beds*, used to filter large quantities of water, sand is the filtering material used, either alone or combined with charcoal or spongy iron. In domestic filters, treating small quantities of water, the filtering material is quartz sand, charcoal, porous stone, or unglazed earthenware or porcelain. Whatever may be the size or construction of the filter, it must be cleaned periodically. If this is neglected the filter ceases to purify the water, and becomes itself a source of contamination. Dissolved organic matter is in part removed by oxidation in filtration through sand filter beds several feet in thickness, or through much thinner layers of charcoal or porous iron. Typhoid and cholera germs pass, although in greatly diminished numbers, through all filters except those made of unglazed porcelain.

Precipitation methods were formerly used only to soften temporarily hard waters. One method consists in the addition of lime water in quantity just sufficient to convert the soluble calcium bicarbonate present into the insoluble carbonate. At present precipitation methods are also used, in combination with

subsidence and **filtration**, to remove organic impurities; alum or a ferric salt is added, an excess being avoided, to form a gelatinous precipitate which carries the impurities down with it mechanically as it settles when the water is left at rest in the subsidence tanks; the water is drawn off from above the deposit to the filters, after a proper interval. **Precipitation** and **subsidence** are thus used to diminish the work required of the filters.

The purification of water by **boiling** can only be carried on on a small scale. It is very useful, however, to soften temporarily hard waters and, particularly, to sterilize infected waters. For the latter purpose the boiling must be continued actively for at least twenty minutes in a vessel closed except for a steam outlet, which is to be stopped with a plug of cotton when the vessel is taken off to cool.

Natural Purification of Water.—The water of brooks, rivers, and lakes which have been contaminated by sewage and other organic impurity becomes gradually purified by natural processes. Suspended particles are deposited upon the bottom and sides of the stream, more or less rapidly, according to their gravity and the rapidity of the current. The bicarbonates of calcium, magnesium, and iron gradually lose carbon dioxide, and are precipitated as carbonates, which mechanically carry down dissolved as well as suspended impurities. The decompositions, oxidations, and reductions to which organic matters are subject under the influence of atmospheric and dissolved oxygen and bacterial action bring about their gradual mineralization by conversion into ammonia and then into nitrates. The processes of nutrition of aquatic plant life absorb dissolved organic impurity, as well as the products of decomposition of nitrogenized substances. This natural purification proceeds the more rapidly the more contact with air is favored.

Mineral Waters.—Under this head are classed all waters which are of therapeutic or industrial value, by reason of the quantity or nature of the dissolved solids which they contain; or which have a temperature greater than 20°.

A useful classification which has been generally adopted includes five classes:

I. *Acidulous waters*; whose value depends upon dissolved carbonic acid. They contain but small quantities of solids, principally the bicarbonates of sodium and calcium and sodium chloride.

II. *Alkaline waters*; which contain quantities of the bicarbonates of sodium, potassium, lithium, and calcium, sufficient to communicate to them an alkaline reaction, and frequently a soapy taste; either naturally, or after expulsion of carbon dioxide by boiling.

III. *Chalybeate waters*; which contain salts of iron in greater proportion than 4 parts in 100,000. They contain ferrous bicarbonate and sulphate, calcium carbonate, sulphates of potassium, sodium, calcium, magnesium, and aluminium, notable quantities of sodium chloride, and frequently small amounts of arsenic. They have the taste of iron and are usually clear as they emerge from the earth. Those containing ferrous bicarbonate deposit a sediment on standing, by loss of carbon dioxide, and formation of ferrous carbonate.

IV. *Saline waters*; which contain neutral salts in considerable quantity. The nature of the salts which they contain is so diverse that the group may well be subdivided:

(a) *Chlorine waters*; which contain large quantities of sodium chloride, accompanied by less amounts of the chlorides of potassium, calcium, and magnesium. Some are so rich in sodium chloride that they are not of service as therapeutic agents, but are evaporated to yield a more or less pure salt. Any natural water containing more than 300 parts in 100,000 of sodium chloride belongs to this class, provided it does not contain substances more active in their medicinal action in such proportion as to warrant its classification elsewhere.

Waters containing more than 1,500 parts in 100,000 are too concentrated for internal administration.

(b) *Sulphate waters* are actively purgative from the presence of considerable proportions of the sulphates of sodium, calcium, and magnesium. Some contain large quantities of sodium sulphate, with mere traces of the calcium and magnesium salts, while in others the proportion of the sulphates of magnesium and calcium is as high as 3,000 parts in 100,000 to 2,000 parts in 100,000 of sodium sulphate. They vary much in concentration; from 500 to nearly 6,000 parts of total solids in 100,000. They have a salty, bitter taste, and vary much in temperature.

(c) *Bromine and Iodine waters* are such as contain the bromides or iodides of potassium, sodium, or magnesium in sufficient quantity to communicate to them the medicinal properties of those salts.

V. *Sulphurous waters*; which hold hydrogen sulphide or metallic sulphides in solution. They have a disagreeable odor and are usually warm. They contain 20 to 400 parts in 100,000 of total solids.

Physiological.—*Water is taken into the body* both as a liquid and as a constituent of every article of food; the amount ingested by a healthy adult being 2.25 to 2.75 litres ($2\frac{1}{3}$ to 3 quarts) a day. The greater the elimination and the drier the nature of the food the greater is the amount of H_2O taken in the liquid form.

Water is a constituent of every tissue and fluid of the body, varying from 0.2 per cent. in the enamel of the teeth to 99.5 per cent. in the perspiration and saliva. It constitutes about 60 per cent. of the weight of the body.

The consistency of the various parts does not depend entirely upon the relative proportion of solids and H_2O , but is influenced by the nature of the solids. The blood, although liquid in the ordinary sense of the term, contains a less proportional amount of H_2O than does the tissue of the kidneys, and about the same proportion as the tissue of the heart. Although the bile and mucus are not as fluid as the blood, they contain a larger proportion of H_2O to solids than does that liquid.

Water is discharged by the kidneys, intestines, skin, and pulmonary surfaces. The quantity discharged is greater than that ingested; the excess being formed in the body by the oxidation of the H of its organic constituents.

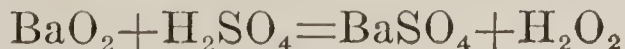
HYDROGEN DIOXIDE.

HYDROGEN PEROXIDE—OXYGENATED WATER.

H_2O_2 —*Molecular weight*=34—*Sp. gr.*=1.455.

Occurrence.—Exists naturally in very minute quantity in rain-water, in air, and in the saliva.

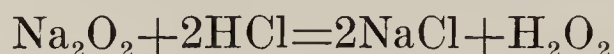
Preparation.—(1) It may be obtained, mixed with a large quantity of H_2O , by the action of dilute mineral acids on barium dioxide:



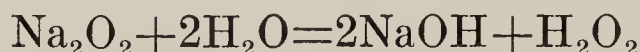
(2) It is also formed in small quantity during the slow oxidation of many elements and compounds, such as P, Pb, Zn, Cd, Al, alcohol, ether and the essences.

(3) It is prepared industrially of 10–12 volume strength by gradually adding barium dioxide to dilute hydrofluoric acid solution, the mixture being maintained at a low temperature and constantly agitated.

(4) In still greater concentration by the action of dilute acids on sodium dioxide, care being had to prevent heating of the mixture:



(5) Hydrogen dioxide is also formed when sodium dioxide is dissolved in water:



Properties.—The pure substance is a colorless, syrupy liquid, which, when poured into H_2O , sinks under it before mixing. It has a disagreeable metallic taste, somewhat resembling that of tartar emetic. When taken into the mouth it produces a tingling sensation, increases the flow of saliva, and bleaches the tissues with which it comes in contact. It is still liquid at -30° . It is very unstable, and, even in darkness and at ordinary temperature, is gradually decomposed. At 20° the decomposition takes place more quickly and at 100° rapidly and with effervescence. The dilute substance, however, is comparatively stable, and may be boiled and even distilled without suffering decomposition. Yet it is liable to explosive decomposition when exposed to summer temperature in closed vessels.

Hydrogen dioxide acts both as a reducing and an oxidizing agent. Arsenic, sulphides, and sulphur dioxide are oxidized by it at the expense of half its oxygen. When it is brought in contact with silver oxide both substances are violently decomposed, water and elementary silver remaining. By certain substances, such as gold, platinum, and charcoal in a state of fine division, fibrin, or manganese dioxide, it is decomposed with evolution of oxygen; the decomposing agent remaining unchanged.

The pure substance, when decomposed, yields 475 times its volume of oxygen; the dilute 15 to 20 volumes.

In dilute solution it is used as a bleaching agent and in the renovation of old oil-paintings. It is an energetic disinfectant and antiseptic, and is used in surgery. “Ozonic ether” is a mixture of ethylic ether and dilute hydrogen dioxide.

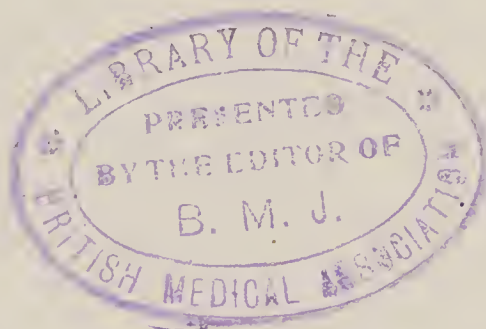
Solution of Hydrogen Dioxide—Liquor Hydrogenii Dioxidi (U. S. P.)—is an aqueous solution containing not less than 3 per cent. by weight of H_2O_2 , and corresponding to not less than 10 volumes of available oxygen.

Analytical Characters.—(1) To a solution of starch a few drops of cadmium iodide solution are added, then a small quantity of the

fluid to be tested, and, finally, a drop of a solution of ferrous sulphate. A blue color is produced in the presence of hydrogen dioxide even if the solution contain only 0.05 milligram per litre.

(2) Add freshly-prepared tincture of guaiacum and a few drops of a cold infusion of malt. A blue color—1 in 2,000,000.

(3) Add to the liquid a few drops of potassium dichromate and a little dilute sulphuric acid, and agitate with ether. The ether assumes a brilliant blue-violet color.



CLASS II.—ELEMENTS WHICH FORM NO COMPOUNDS.

HELIUM. NEON. ARGON. KRYPTON. XENON. NITON.

The elements of this group have been recently discovered, and exist in air and in certain minerals. As they form no compounds, their atomic weights are not known, although, from their molecular heats, there is reason to believe that their molecular symbols are He, etc., not He_2 , etc.

Argon, the most abundant of the class, was discovered by Rayleigh and Ramsay in 1894 in air, in which it exists in the proportion of 0.9 in 100 by volume, and 1.2 per cent. by weight. It is a transparent, colorless, odorless, tasteless gas; sp. gr.=19.941; Mw.=40 (International=39.88). At the normal pressure it liquefies at -186.9° , forming a colorless liquid of sp. gr. 1.5. It solidifies at -190° . It is sparingly soluble in water: 4.05 in 100. It is obtained from atmospheric air as a residue by causing the other constituents to enter into combination. When rarefied it gives a characteristic spectrum of many lines with the induction spark.

Helium owes its name to the fact that its existence in the sun's atmosphere was recognized by the characteristic line D_3 of the solar spectrum before it was discovered as a terrestrial element. It exists in certain rare uranium minerals, and in some spring waters. It is a very light gas: Mw.=4.

The other members of the class: **Neon**: Mw.=20 (International=20.2); **Krypton**: Mw.=83 (International=82.92); and **Xenon**: Mw.=130 (International=130.2), have been found in small amount in the residue of evaporation of liquefied air.

Niton: Mw.=222 (International=222.4), radium emanation, also belongs to this group.

It has been estimated that these gases are present in air, in about the following proportions:

Argon	0.9 part in	100 of air.
Neon	1 to 2 parts in	100,000 of air.
Krypton	1 part in	1,000,000 of air.
Helium	1 to 2 parts in	1,000,000 of air.
Xenon	1 part in	20,000,000 of air.

CLASS III.—ACIDULOUS ELEMENTS.

Elements all of whose Hydrates are Acids and which do not form Salts with the Oxyacids.

I. CHLORINE GROUP.

FLUORINE. CHLORINE. BROMINE. IODINE.

The elements of this group, known as the **halogens**, closely resemble each other in their chemical properties and in the structure and properties of their compounds, fluorine differing more from the other three than these do from each other. They are univalent in the great majority of the compounds into whose formation they enter, although they are sometimes trivalent, as in ICl_3 . With hydrogen each forms an acid compound, composed of one volume of the halogen in the gaseous state with one volume of hydrogen. All mineral acids into whose composition they enter are monobasic. Fluorine is a gas, liquefiable with difficulty, chlorine an easily liquefiable gas, bromine a liquid, and iodine a solid at the ordinary temperature and pressure. The relations of their compounds to each other are shown in the following table:

HF	_____	_____	_____	_____	_____	_____
HCl	Cl_2O	Cl_2O_4	HClO	HClO_2	HClO_3	HClO_4
HBr	_____	_____	HBrO	_____	HBrO_3	HBrO_4
HI	_____	I_2O_4	HIO	HIO_2	HIO_3	HIO_4
Hydro-ic acid.	Monoxide.	Tetroxide.	Hypo- ous acid.	-ous acid.	-ic acid.	Per-ic acid.

FLUORINE.

Symbol=F—*Atomic weight*=19 (*International*=19.0).—*Molecular weight*=38.—*Sp. gr.* 1.265 A (*calculated*=1.316).

Fluorine has been isolated by the electrolysis of pure, dry HF at -23° . It exists in nature chiefly in *Fluor-Spar*, CaF_2 , and in *cryolite*, $\text{Al}_2\text{F}_6 (\text{NaF})_6$.

It is a gas, colorless in thin layers, greenish yellow in thick layers. It decomposes H_2O , with formation of HF and ozone. In it Si, B, As, Sb, S, and I fire spontaneously. With H it detonates, even in the dark. It attacks organic substances violently. The apparatus in which it is liberated must be made of platinum or fluor-spar. It forms compounds with all other elements except oxygen.

Hydrogen Fluoride.—*Hydrofluoric acid*=HF—*Molecular weight*=20. Hydrofluoric acid is obtained by the action of an excess of

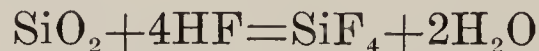
sulphuric acid upon fluor-spar or upon barium fluoride, with the aid of gentle heat:



If a solution is desired, the operation is conducted in a platinum or lead retort, whose beak is connected with a U-shaped receiver of the same metal, which is cooled and contains a small quantity of water.

The pure acid is a colorless liquid, which boils at 19° and solidifies at -1° . Sp. gr. 0.985 at 12° . The aqueous acid is a colorless liquid, highly acid and corrosive, and having a penetrating odor. Great care must be exercised that neither the solution nor the gas comes in contact with the skin, as they produce painful ulcers which heal with difficulty, and also constitutional symptoms which may last for days. The inhalation of air containing very small quantities of HF has caused permanent loss of voice, and in rare cases, death. When the acid has accidentally come in contact with the skin the part should be washed with dilute solution of potassium hydroxide, and the vesicle which forms should be opened.

Both the gaseous acid and its solution remove the silica from glass, a property utilized in etching upon that substance, the parts upon which no action is desired being protected by a coating of wax. During the process of etching the HF attacks the silica and forms a gaseous silicon fluoride:



Test.—The presence of fluorine in a compound is detected by reducing the substance to powder, moistening it with sulphuric acid in a platinum crucible, over which is placed a slip of glass prepared as above. At the end of half an hour the wax is removed from the glass, which will be found to be etched if the substance examined contained a fluoride.

CHLORINE.

Symbol=Cl—*Atomic weight*=35.5 (*International*=35.46)—*Molecular weight*=71—*Sp. gr.*=2.4502 A.

Occurrence.—Only in combination, most abundantly in sodium chloride; the chlorides of potassium, calcium, and magnesium are also frequently found in nature.

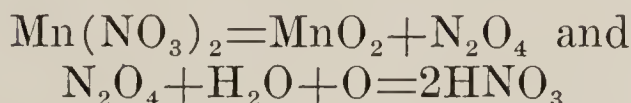
Preparation.—(1) By heating together manganese dioxide and hydrochloric acid:



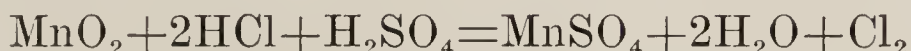
In a modification of this process, which permits of the more easy recovery of the manganese dioxide, nitric acid is used along with hydrochloric. The reaction is:



The MnO_2 and HNO_3 are recovered by heating the manganese nitrate to 190° and treating the vapor with air and steam. The reactions are:

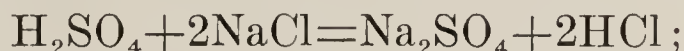


(2) By the action of manganese dioxide upon hydrochloric acid in the presence of sulphuric acid, manganous sulphate being also formed:



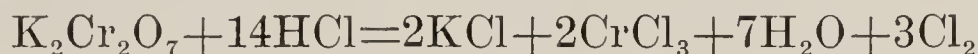
The same quantity of chlorine is obtained as in (1), with the use of half the amount of hydrochloric acid.

(3) By heating a mixture of one part each of manganese dioxide and sodium chloride, with three parts of sulphuric acid. Hydrochloric acid and sodium sulphate are first formed:

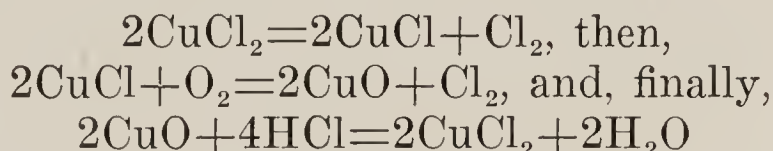


and the acid is immediately decomposed by either of the reactions indicated in (1) and (2), according as sulphuric acid is or is not present in excess.

(4) By the action of potassium dichromate upon hydrochloric acid; potassium and chromic chlorides being also formed:



(5) In Deacon's process cupric oxide is used as a "contact substance" to oxidize hydrochloric acid. The reactions are:



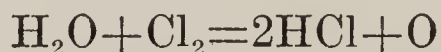
As the O is derived from air the Cl obtained is largely diluted with N.

Properties.—*Physical.*—It is about $2\frac{1}{2}$ times heavier than air; it is a greenish yellow gas, at the ordinary temperature and pressure; it has a penetrating odor, and is, even when highly diluted, very irritating to the respiratory passages. Being soluble in H_2O to the extent of one volume to three volumes of the solvent, it must be collected by displacement of air. An aqueous solution containing, when freshly made, a mixture of chlorine and oxides of chlorine, equivalent to about 0.35 gm. of available chlorine in each 100 cc. of the solution is known as **chlorine water**, and is official in the U. S. P. as **Liquor chlori compositus**. It should bleach, but not redden, litmus paper. Under a pressure of 6 atmospheres at 0° , or $8\frac{1}{2}$ atmospheres at 12° , Cl becomes an oily, yellow liquid, of sp. gr. 1.33; and boiling at -33.6° . Liquid chlorine, transported in lead-lined steel cylinders, is now an article of commerce.

Chemical.—Chlorine exhibits a great tendency to combine with other elements, with all of which, except F, O, N, and C, it unites directly, frequently with evolution of light as well as heat, and sometimes with an explosion. With H it combines slowly, to form hydrochloric acid, under the influence of diffuse daylight, and violently in direct sunlight, or in highly actinic artificial lights. A candle burns in Cl with a faint flame and thick smoke, its H combining with the Cl, while carbon becomes free.

At a red heat Cl decomposes H_2O rapidly, with formation of hydrochloric, chloric, and probably hypochlorous acids. The same change takes place slowly under the influence of sunlight, hence chlorine water should be kept in the dark or in bottles of yellow glass.

In the presence of H_2O , chlorine is an active bleaching and disinfecting agent. It acts as an indirect oxidant, decomposing H_2O , the nascent O from which then attacks the coloring or odorous principle:



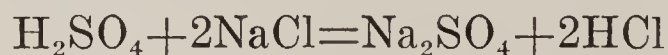
Chlorine is readily fixed by many organic substances, either by addition or substitution. In the first instance, as when Cl and olefiant gas unite to form ethylene chloride, the organic substance simply takes up two or more atoms of chlorine: $C_2H_4 + Cl_2 = C_2H_4Cl_2$. In the second instance, as when Cl acts upon marsh gas to produce methyl chloride: $CH_4 + Cl_2 = CH_3Cl + HCl$, each substituted atom of Cl displaces an atom of H, which combines with another Cl atom to form hydrochloric acid.

Hydrogen Chloride — Hydrochloric Acid — Muriatic Acid —
Acidum Hydrochloricum (U. S. P.)—HCl—Molecular weight=
36.5—Sp. gr. 1.259 A.

Occurrence.—In volcanic gases and in the gastric juice of the mammalia.

Preparation.—(1) By the direct union of its constituent elements.

(2) By the action of sulphuric acid upon a chloride, a sulphate being at the same time formed:



This is the reaction by which HCl used in the arts is produced.

(3) Hydrochloric acid is also formed in a great number of reactions, as when Cl is substituted in an organic compound.

Properties.—*Physical.*—A colorless gas, acid in reaction and taste, having a sharp, penetrating odor, and producing great irritation when inhaled. It becomes liquid under a pressure of 40 atmospheres at 4° . Its critical temperature is 52° and its critical pressure 83 atmospheres. It is very soluble in H_2O , one volume of which dissolves 480 volumes of the gas at 0° .

Chemical.—Hydrochloric acid is neither combustible nor a sup-

porter of combustion, although certain elements, such as K and Na, burn in it. It forms white clouds on contact with moist air.

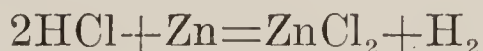
Solution of Hydrochloric Acid.—It is in the form of aqueous solution that this acid is usually employed in the arts and in pharmacy. It is, when pure, a colorless liquid (yellow when impure), acid in taste and reaction, whose sp. gr. and boiling-point vary with the degree of concentration. When heated, it evolves HCl, if it contain more than 20 per cent. of that gas, and H₂O if it contain less. A solution containing 20 per cent. boils at 111°, is of sp. gr. 1.099, has the composition HCl+8H₂O, and distils unchanged.

Commercial muriatic acid is a yellow liquid; sp. gr. about 1.16; contains 32 per cent. HCl; and contains ferric chloride, sodium chloride, and arsenical compounds.

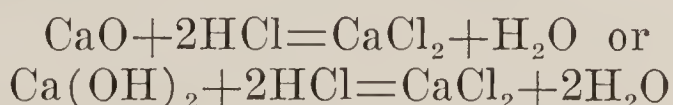
Acidum hydrochloricum is a colorless liquid, containing small quantities of impurities. It contains not less than 31 per cent. nor more than 33 per cent. HCl and its sp. gr. is about 1.155 at 25°C. (U. S. P.) The dilute acid is the above diluted with water. Sp. gr. 1.049—not less than 9.5 per cent. nor more than 10.5 per cent. HCl (U. S. P.).

C. P. (chemically pure) acid is usually the same as the strong pharmaceutical acid and far from pure (see below). The strongest solution has a sp. gr. of 1.20 and contains 40.8 per cent. HCl.

Hydrochloric acid is classed, along with nitric and sulphuric acids, as one of three **strong mineral acids**. It is decomposed by many elements, with formation of a chloride and liberation of hydrogen:



With oxides and hydroxides of the metals it enters into double decomposition, forming H₂O and a chloride:



Oxidizing agents decompose HCl with liberation of Cl. A mixture of hydrochloric and nitric acids in the proportion of three molecules of the former to one of the latter (18 cc. HNO₃: 82 cc. HCl soln.), is the **acidum nitrohydrochloricum** (*nitrohydrochloric acid, nitromuriatic acid*) of the U. S. P., or **aqua regia** (see p. 102). The latter name alludes to its power of dissolving gold, by combination of the nascent Cl, which it liberates, with that metal, to form the soluble auric chloride (p. 129). The U. S. P. also includes *acidum nitrohydrochloricum dilutum* (*diluted nitrohydrochloric acid, diluted nitromuriatic acid*), which contains 10 cc. HNO₃; 45.5 cc. HCl; and 194.5 cc. H₂O.

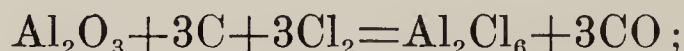
Impurities.—A chemically pure solution of this acid is exceedingly rare. The impurities usually present are: *Sulphurous acid*—hydrogen sulphide is given off when the acid is poured upon zinc; *Sulphuric acid*—a white precipitate is

formed with barium chloride; *Chlorine* colors the acid yellow; *Lead* gives a black color when the acid is treated with hydrogen sulphide; *Iron*—the acid gives a red color with ammonium thiocyanate; *Arsenic*—the method of testing by hydrogen sulphide is not sufficient. If the acid is to be used for toxicological analysis, a litre, diluted with half as much H_2O , and to which a small quantity of potassium chlorate has been added, is evaporated over the water bath to 400 cc.; 25 cc. of sulphuric acid are then added, and the evaporation continued until the liquid measures about 100 cc. This is introduced into a Marsh apparatus and must produce *no* mirror during an hour.

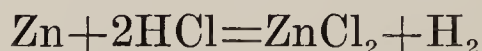
Chlorides.—A few of the chlorides are liquid, $SnCl_4$, $SbCl_5$; the remainder are solid, crystalline and more or less volatile. The metallic chlorides are soluble in water, except $AgCl$ and $HgCl$, which are insoluble, and $PbCl_2$, and $CuCl$, which are sparingly soluble. The chlorides of the non-metals are decomposed by H_2O .

The chlorides are formed: (1) By direct union of the elements:
 $P + Cl_5 = PCl_5$;

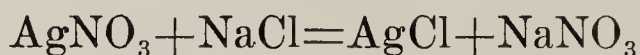
(2) By the action of chlorine upon a heated mixture of oxide and carbon:



(3) By solution of the metal, oxide, hydroxide, or carbonate in HCl :



(4) By double decomposition between a solution of a chloride and that of another salt whose metal forms an insoluble chloride:



Chloridion—Analytical Characters.—Solutions of hydrochloric acid and of chlorides contain the ion, chloridion Cl' , which gives the following reactions: (1) With $AgNO_3$ a white, flocculent ppt., insol. in HNO_3 , sol. in NH_4OH . (2) With $HgNO_3$, a white ppt., which turns black with NH_4OH .

Toxicology.—Poisons and Corrosives.—A poison is any substance which, being in solution in, or acting chemically upon the blood, may produce death or serious bodily harm.

A corrosive is a substance capable of producing death by its chemical action upon a tissue with which it comes in direct contact.

The corrosives act much more energetically when concentrated than when dilute; and when the dilution is great they have no deleterious action. The degree of concentration in which the true poisons are taken is of little influence upon their action.

Under the above definitions the strong mineral acids act as corrosives rather than as poisons. They produce their injurious results by destroying tissues with which they come in contact, and will cause death as surely by destroying a large surface of skin as when they are taken into the stomach.

The *symptoms of corrosion by the mineral acids* begin immediately, during the act of swallowing. The chemical action of the acid upon every part with which it comes in contact causes acute burning pain, extending from the mouth

to the stomach and intestine, referred chiefly to the epigastrium. Violent and distressing vomiting of dark, tarry, or "coffee-ground," highly acid material is a prominent symptom. Eschars, at first white or gray, later brown or black, are formed where the acid has come in contact with the skin or mucous membrane. Respiration is labored and painful, partly by pressure of the abdominal muscles, but also, in the case of hydrochloric acid, from entrance of the irritating gas into the respiratory passages. Death may occur within twenty-four hours, from collapse; more suddenly from perforation of large blood-vessels, or from peritonitis; or after several weeks, secondarily, from starvation, due to closure of the pylorus by inflammatory thickening, and destruction of the gastric glands.

The object of *the treatment in corrosion by the mineral acids* is to neutralize the acid and convert it into a harmless salt. For this purpose the best agent is calcined magnesia, suspended in a small quantity of water, or if this is not at hand, a strong solution of soap. Chalk and the carbonates and bicarbonates of sodium and potassium should not be given, as they generate large volumes of gas. The scrapings of a plastered wall, or oil, are entirely useless. Any attempt at the introduction of a tube into the esophagus is attended with danger of perforation, except in the earliest stages of the intoxication.

Compounds of Chlorine and Oxygen.—Two compounds of chlorine and oxygen are known. They are both very unstable, and prone to sudden violent decomposition.

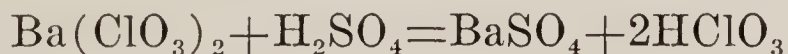
Chlorine Monoxide.— Cl_2O —87—*Hypochlorous anhydride*, is formed by the action, below 20° , of dry Cl upon precipitated mercuric oxide: $\text{HgO} + 2\text{Cl}_2 = \text{HgCl}_2 + \text{Cl}_2\text{O}$.

On contact with H_2O it forms **hypochlorous acid**, HClO , which owing to its instability, is not used industrially, although the hypochlorites of Ca, K, and Na are.

Chlorine Tetroxide.—*Chlorine peroxide*, Cl_2O_4 —135—is a violently explosive body, produced by the action of sulphuric acid upon potassium chlorate. Below -20° it is an orange-colored liquid, above that temperature a yellow gas. It explodes violently when heated to a temperature below 100° . There is no corresponding hydrate known, and if it be brought in contact with an alkaline hydroxide, a mixture of chlorate and chloride is formed.

Besides the above, two oxyacids of Cl are known, the anhydrides corresponding to which have not been isolated.

Chloric Acid— HClO_3 —84.5—obtained, in aqueous solution, as a strongly acid, yellowish, syrupy liquid, by decomposing barium chlorate by sulphuric acid:



Perchloric Acid.— HClO_4 —100.5—is the most stable of the series. It is obtained by boiling potassium chlorate with hydrofluosilicic acid, decanting the cold fluid, evaporating until white fumes appear, decanting from time to time, and finally distilling. It is a colorless, oily liquid; sp. gr. 1.782; which explodes on contact with organic substances or charcoal.

BROMINE.

Symbol=Br.—*Atomic weight*=80—(*International*=79.92)—*Molecular weight*=160—*Sp. gr. of liquid*=3.1872 at 0°; *of vapor*=5.52 A.

Occurrence.—Only in combination, most abundantly with Na, K, Ca, and Mg in sea water and the waters of mineral springs.

Preparation.—It is obtained from the mother liquors, left by the evaporation of sea water, and of that of certain mineral springs, and from sea weed.

Bromine may be prepared from the bromide of Na or K by heating with sulphuric acid and manganese dioxide:



Properties.—*Physical.*—A dark reddish-brown liquid, volatile at all temperatures above -24.5° ; giving off brown-red vapors which produce great irritation when inhaled. Soluble in water to the extent of 3.2 parts per 100 at 15° ; more soluble in alcohol, carbon disulphide, chloroform, and ether.

Chemical.—The chemical characters of Br are similar to those of Cl, but less active.—With H_2O it forms a crystalline hydrate at 0° (32° F): $\text{Br} \cdot 5\text{H}_2\text{O}$. Its aqueous solution is decomposed by exposure to light, with formation of hydrobromic acid.

It is highly poisonous.

Hydrogen Bromide — Hydrobromic acid. = HBr — *Molecular weight*=81. *Sp. gr.* 2.71 A.

Preparation.—This substance cannot be obtained from a bromide as HCl is obtained from a chloride. It is produced, along with phosphorous acid, by the action of H_2O upon phosphorus tribromide:

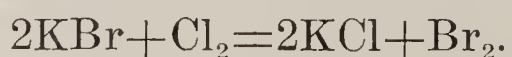


or by the action of Br upon paraffin.

Properties.—A colorless gas; produces white fumes with moist air; acid in taste and reaction, and readily soluble in H_2O , with which it forms a hydrate, $\text{HBr} \cdot 2\text{H}_2\text{O}$. Its chemical properties are similar to those of HCl .

The **Acidum hydrobromicum dilutum** of the U. S. P. (*dilute hydrobromic acid*) contains not less than 9.5 per cent. nor more than 10.5 per cent. of HBr .

Bromides closely resemble the chlorides and are formed under similar conditions. They are decomposed by chlorine, with formation of a chloride and liberation of Br:



The metallic bromides are soluble in H_2O , except AgBr and HgBr ,

which are insoluble, and PbBr_2 , which is sparingly soluble. The bromides of Mg, Al, Ca are decomposed into oxide and HBr on evaporation of their aqueous solutions.

Bromidion—Analytical Characters.—Solutions of hydrobromic acid and of bromides contain the anion Br' , which gives the following reactions: (1) With AgNO_3 , a yellowish white ppt., insoluble in HNO_3 , sparingly soluble in NH_4OH . (2) With chlorine water a yellow solution which communicates the same color to chloroform and to starch-paste.

Hypobromous Acid— HBrO —97—is obtained, in aqueous solution, by the action of Br upon mercuric oxide, silver oxide, or silver nitrate. When Br is added to concentrated solution of potassium hydroxide no hypobromite is formed, but a mixture of bromate and bromide, having no decolorizing action. With sodium hydroxide, however, sodium hypobromite is formed in solution; and such a solution, freshly prepared, is used in Knop's process for determining urea.

IODINE.

Iodum (U. S. P.)—*Symbol*=I—*Atomic weight*=127 (*International*=126.92). *Molecular weight*=254—*Sp. gr. of solid*=4.948; *of vapor*=8.716 A.

Occurrence.—In combination with Na, K, Ca, and Mg, in seawater, the waters of mineral springs, marine plants and animals. Cod-liver oil contains about 37 parts in 100,000.

Preparation.—It is obtained from the ashes of sea-weed, called *kelp* or *varech*. These are extracted with H_2O , and the solution evaporated to small bulk. The mother liquor, when separated from the other salts which crystallize out, contains the iodides, which are decomposed by Cl, aided by heat, and the liberated iodine is condensed.

Iodine may be prepared from the iodide of Na or K by heating with sulphuric acid and manganese dioxide:



Properties.—Physical.—Blue-gray, crystalline scales, having a metallic luster. Volatile at all temperatures, the vapor having a violet color and a peculiar odor. The density of vapor of iodine, at one atmosphere of pressure and at temperatures between its boiling point and about 500° is 254 ($\text{O}=32$), corresponding to the molecular formula I_2 , but above that temperature the density diminishes, until at $1,500^\circ$ it has fallen to 127, corresponding to the molecular formula I, where it remains constant. Molecular iodine is, therefore, dissociated by heat. Iodine is very sparingly soluble in water, but the aqueous solution, standing over excess of iodine, continues to dissolve it by reason of the formation of hydriodic acid. Solutions of hydriodic acid and of metallic iodides dissolve notably larger quantities of iodine than does pure water, probably because of the forma-

tion of the ion I_3' . *Lugol's solution*—*Liquor iodi compositus* (U. S. P.)—contains 5 parts of iodine and 10 parts of potassium iodide in 100 parts of water. Iodine is very soluble in alcohol, ether, chloroform, benzene and carbon disulphide. With the three last named solvents the solutions are violet, with others brown in color.

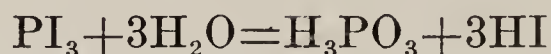
Chemical.—In its chemical characters I resembles Cl and Br, but is less active. It decomposes H_2O slowly and is a weak bleaching and oxidizing agent. In presence of water, it decomposes hydrogen sulphide with formation of hydriodic acid, and liberation of sulphur. It does not combine directly with oxygen, but does with ozone. Potassium hydroxide solution dissolves it, with formation of potassium iodide, and some hypoiodite. Nitric acid oxidizes it to iodic acid. With ammonium hydroxide solution it forms the explosive nitrogen iodide.

Toxicology.—Taken internally, iodine acts both as a local irritant and as a true poison. It is discharged as an alkaline iodide by the urine and perspiration, and when taken in large quantity it appears in the feces.

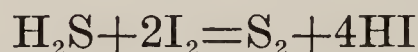
The poison should be removed as rapidly as possible by the use of the stomach tube and of emetics. Farinaceous substances may also be given.

Hydrogen Iodide—Hydriodic acid—HI—Molecular weight=128.

Preparation.—By the decomposition of phosphorus triiodide by water:



Or, in solution by passing hydrogen sulphide through water holding iodine in suspension:



Properties.—A colorless gas, forming white fumes on contact with air, and of strongly acid reaction. Under the influence of cold and pressure it forms a yellow liquid, which solidifies at -55° . Water dissolves it to the extent of 425 volumes for each volume of the solvent at 10° .

It is partly decomposed into its elements by heat. Mixed with O it is decomposed, even in the dark, with formation of H_2O and liberation of I. Under the influence of sunlight the gas is slowly decomposed, although its solutions are not so affected, if they be free from air. Chlorine and bromine decompose it, with liberation of iodine. With many metals it forms iodides. It yields up its H readily and is used in organic chemistry as a source of that element in the nascent state.

The *Acidum hydriodicum dilutum* (*diluted hydriodic acid*) of the U. S. P. contains not less than 9.5 per cent. nor more than 10.5 per cent. of HI.

Iodides are formed under the same conditions as the chlorides and bromides, which they resemble in their properties. The metallic

iodides are soluble in water—except AgI, HgI, which are insoluble, and PbI₂, which is very slightly soluble. The iodides of the earth metals are decomposed into oxide and HI on evaporation of their aqueous solutions. Chlorine decomposes the iodides as it does the bromides.

Iodidion—Analytical Characters.—Solutions of hydriodic acid or of iodides contain iodidion, I', which forms a yellow ppt., insol. in HNO₃ and in NH₄OH, with Ag'NO₃. Brown solutions of excess of iodine in HI or KI contain triiodidion, I₃', which, as iodine is removed from the solution, is decomposed into I' + I₂. Aqueous or alcoholic solutions of free iodine, not of iodidion, color starch paste dark blue or black, and chloroform or carbon bisulphide violet. The same colors are produced with solutions of iodides after liberation from them of free iodine by fuming HNO₃ or chlorine water. At about 100° starch iodide is dissociated and decolorized, the color returning on cooling.

Chlorides of Iodine.—Chlorine and iodine combine with each other in two proportions: **Iodine monochloride**, or **protochloride**—ICl is a red-brown, oily, pungent liquid, formed by the action of dry Cl upon I, and distilling at 100°. **Iodine trichloride**, or **perchloride**—ICl₃ is a yellow, crystalline solid, having an astringent, acid taste and a penetrating odor; very volatile; its vapor irritating; easily soluble in water. It is formed by saturating H₂O holding I in suspension with Cl, and adding concentrated sulphuric acid. ICl₃ has been used as an antiseptic.

Oxyacids of Iodine.—The best known of these are the highest two of the series—iodic and periodic acids.

Iodic Acid—HIO₃—176 is formed as an iodate, whenever I is dissolved in a solution of an alkaline hydroxide:



As the free acid, by the action of strong oxidizing agents, such as nitric acid, or chloric acid, upon I; or by passing Cl for some time through H₂O holding I in suspension.

Iodic acid appears in white crystals, decomposable at 170°, and quite soluble in H₂O, the solution having an acid reaction, and a bitter, astringent taste.

It is an energetic oxidizing agent, yielding up its O readily, with separation of elementary I or of HI. It is used as a test for the presence of morphine.

Periodic Acid—HIO₄—192—is formed by the action of Cl upon an alkaline solution of sodium iodate. The sodium salt thus obtained is dissolved in nitric acid, treated with silver nitrate, and the resulting silver periodate is then decomposed with H₂O. From the solution the acid is obtained in colorless crystals, fusible at 130°, very soluble in water, and readily decomposable by heat.

II. SULPHUR GROUP.

SULPHUR. SELENIUM. TELLURIUM.

The elements of this group are bivalent in most of their compounds; in some they are quadrivalent or hexavalent. With hydrogen they form compounds composed of one volume of the element, in the

form of vapor, with two volumes of hydrogen—the combination being attended with condensation in volume of one-third. Mineral acids in which they occur are dibasic. They are all solids at ordinary temperatures. The relation of their compounds to each other is shown in the following table:

H_2S	SO_2	SO_3	H_2SO_2	H_2SO_4	H_2SO_4
H_2Se	SeO_2	SeO_3	————	H_2SeO_3	H_2SeO_4
H_2Te	TeO_2	TeO_3	————	H_2TeO_3	H_2TeO_4
Hydro-ic acid.	Dioxide.	Trioxide.	Hypo-ous acid.	-ous acid.	-ic acid.

SULPHUR.

Symbol=S—*Atomic weight*=32 (*International*=32.06). *Molecular weight*=64—*Sp. gr. of vapor*=2.22 A.

Occurrence.—Free in crystalline powder, large crystals, or amorphous, in volcanic regions. In *combination* in sulphides and sulphates, and in protein substances.

Preparation.—By purification of the native sulphur or decomposition of *pyrites*, natural sulphides of iron.

Crude sulphur is the product of the first distillation. A second distillation, in more perfectly constructed apparatus, yields *refined sulphur*. During the first part of the distillation, while the air of the condensing chamber is still cool, the vapor of S is suddenly condensed into a fine, crystalline powder, which is **flowers of sulphur**, **sulphur sublimatum** (*sublimed sulphur*) (U. S. P.). Later, when the temperature of the condensing chamber is about 114° , the liquid S collects at the bottom, whence it is drawn off and cast into sticks of **roll sulphur**.

Properties.—*Physical.*—Sulphur, also known as **brimstone**, is usually yellow in color. At low temperature, and in minute subdivision, as in the precipitated **milk of sulphur**, **sulphur præcipitatum** (U. S. P.), it is almost quite colorless. Its taste and odor are faint but characteristic. At 114° it fuses to a thin yellow liquid, which at 150° – 160° becomes thick and brown; at 330° – 340° it again becomes thin and light in color; finally it boils, giving off brownish yellow vapor at a temperature variously stated between 440° and 448° . If heated to about 400° and suddenly cooled, it is converted into **plastic sulphur**, which may be moulded into any desired form. It is insoluble in water, sparingly soluble in aniline, phenol, benzene, petroleum ether, and chloroform; readily soluble in sulphur chloride, S_2Cl_2 , and carbon disulphide. It dissolves in hot alcohol, and crystallizes from the solution, on cooling, in white prismatic crystals. It is dimorphous. When fused sulphur crystallizes it does so in oblique rhombic prisms. Its solution in carbon disulphide deposits it on evaporation in rhombic octahedra. The prismatic variety is of sp. gr. 1.95 and fuses at 120° ; the sp. gr. of the octahedral is 2.05 and

its fusing point 114.5° . The prismatic crystals, by exposure to air, become opaque, by reason of a gradual conversion into octahedra.

Chemical.—Sulphur unites readily with other elements, especially at high temperatures. Heated in air or O, it burns with a blue flame to sulphur dioxide, SO_2 . In H it burns with formation of hydrogen sulphide, H_2S . The compounds of S are similar in constitution, and to some extent in chemical properties, to those of O. In many organic substances S may replace O, as in thiocyanic acid, CNSH , corresponding to cyanic acid, CNOH . Such compounds are designated by the syllable *thio*; the syllable *sulpho*, in the name of a compound, indicates that it contains the bivalent group, SO_2 .

Sulphur is used principally in the manufacture of gunpowder; also to some extent in making sulphuric acid, sulphur dioxide, and matches, and for the prevention of fungoid and parasitic growths.

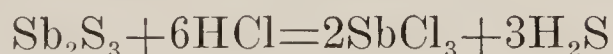
Hydrogen Sulphide — sulphuretted hydrogen — Sulphydric acid— H_2S —*Molecular weight*=34—*Sp. gr.*=1.19 A.

Occurrence.—In volcanic gases; as a product of the decomposition of organic substances containing S; in solution, in the waters of some mineral springs; and, occasionally, in small quantity, in the gases of the intestine. It is produced from proteins and other organic substances containing S by microbic action (sulphydric fermentation).

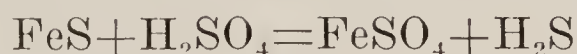
Preparation.—(1) By direct union of the elements; either by burning S in H, or by passing H through molten S.

(2) By the action of nascent H upon sulphuric acid, if the mixture become heated. (See Marsh test for arsenic.)

(3) By the action of HCl upon antimony trisulphide:



(4) By the action of dilute sulphuric acid upon ferrous sulphide:



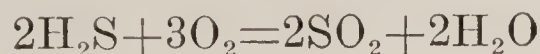
This is the method generally used.

(5) By the action of HCl upon calcium sulphide:

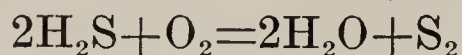


Properties.—*Physical.*—A colorless gas having the odor of rotten eggs and a disgusting taste; soluble in H_2O to the extent of 3.23 parts to 1 at 15° ; soluble in alcohol. Under 17 atmospheres pressure, or at -74° at the ordinary pressure, it liquefies; at -85.5° it forms white crystals.

Chemical.—Burns in air with formation of sulphur dioxide and water:



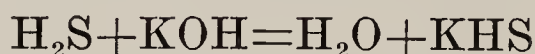
If the supply of oxygen is deficient, H_2O is formed, and sulphur liberated:



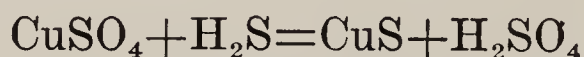
Mixtures of H_2S and air or O explode on contact with flame. Solutions of the gas when exposed to air become oxidized with deposition of S . Such solutions should be made with boiled H_2O , and kept in bottles which are completely filled, and well corked. Oxidizing agents, Cl , Br , and I remove its H with deposition of S . Hydrogen sulphide and sulphur dioxide mutually decompose each other into water, pentathionic acid and sulphur:



When the gas is passed through a solution of an alkaline hydroxide its S displaces the O of the hydroxide to form a sulphhydrate:



With solutions of metallic salts H_2S usually relinquishes its S to the metal:



a property which renders it of great value in analytical chemistry.

Physiological.—Hydrogen sulphide is produced in the intestine

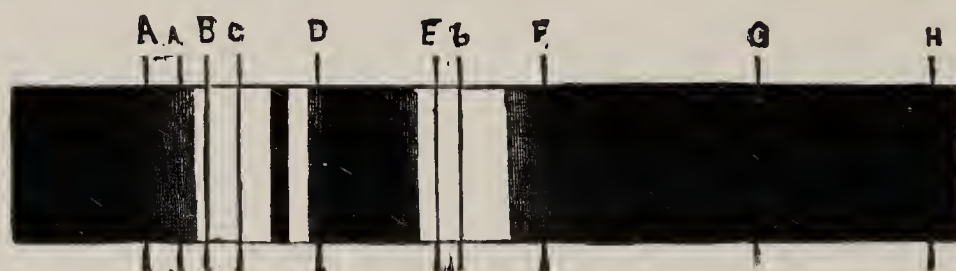


FIG. 12.

by the decomposition of protein substances or of taurochloric acid; it also occurs sometimes in abscesses, and in the urine in tuberculosis, variola, and cancer of the bladder. It may also reach the bladder by diffusion from the rectum.

Toxicology.—An animal dies almost immediately in an atmosphere of pure H_2S , and the diluted gas is still rapidly fatal. An atmosphere containing 1 per cent. may be fatal to man, although individuals habituated to its presence can exist in an atmosphere containing 3 per cent. Its toxic powers are due primarily, if not entirely, to its power of reducing and combining with the blood-coloring matter.

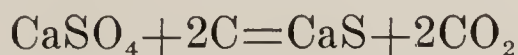
The form in which hydrogen sulphide generally produces deleterious effects is as a constituent of the gases emanating from sewers, privies, burial vaults, etc. These give rise to either slow poisoning, as when sewer gases are admitted to sleeping and other apartments by defective plumbing, or to sudden poisoning, as when a person enters a vault or other locality containing the noxious atmosphere.

The *treatment* should consist in promoting the inhalation of pure air, artificial respiration, cold affusions, and the administration of stimulants.

After death the blood is found to be dark in color, and gives the spectrum shown in Fig. 12, due to sulphemoglobin.

Sulphides and Hydrosulphides.—These compounds bear the same relation to sulphur that the oxides and hydroxides do to oxygen. The two sulphides of arsenic, As_2S_3 and As_2S_5 , correspond to the two oxides, As_2O_3 and As_2O_5 , and the potassium hydrosulphide, KHS , corresponds to the hydroxide, KOH .

Many metallic sulphides occur in nature, and are important ores of the metals, as the sulphide of zinc, mercury, cobalt, nickel, and iron. They are formed artificially, either by direct union of the elements at elevated temperatures, as in the case of iron: $\text{Fe} + \text{S} = \text{FeS}$; or by reduction of the corresponding sulphate, as in the case of calcium:



The sulphides are insoluble in H_2O , except those of the alkali metals. Many of the sulphides are soluble in alkaline liquids, and behave as **thio-anhydrides**, forming thio-salts, corresponding to the oxysalts. Thus potassium arsenate, K_3AsO_4 , and thioarsenate, K_3AsS_4 ; antimonate, K_3SbO_4 , and thioantimonate, K_3SbS_4 .

The metallic sulphides are decomposed when heated in air, usually with the formation of sulphur dioxide and the metallic oxide; sometimes with the formation of the sulphate; and sometimes with the liberation of the metal, and the formation of sulphur dioxide. The strong mineral acids decompose the sulphides with the formation of hydrogen monosulphide.

Analytical Characters.—*Hydrogen Sulphide.*—(1) Blackens paper moistened with lead acetate solution. (2) Has an odor of rotten eggs.

Sulphides.—(1) Heated in the oxidizing flame of the blowpipe, give a blue flame and odor of SO_2 . (2) With a mineral acid give off H_2S (except sulphides of Hg , Au , and Pt).

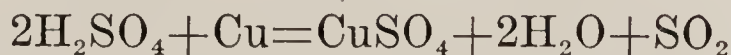
Sulphur Dioxide.—*Sulphurous oxide*, or *anhydride*— SO_2 —*Molecular weight*=64—*Sp. gr. of gas*=2.213; *of liquid*=1.45.

Occurrence.—In volcanic gases and in solution in some mineral waters.

Preparation.—(1) By burning S in air or O .

(2) By roasting iron pyrites in a current of air.

(3) By heating sulphuric acid with copper:



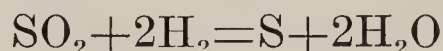
(4) By heating sulphuric acid with charcoal:



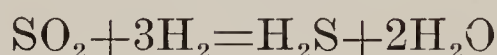
When the gas is to be used as a disinfectant it is usually obtained by reaction (1); in sulphuric acid factories (2) is used; in the laboratory (3) is used.

Properties.—*Physical.*—A colorless, suffocating gas, having a disagreeable and persistent taste. Very soluble in H_2O , which at 15° dissolves about 40 times its volume (see below); also soluble in alcohol. At -10° it forms a colorless, mobile, transparent liquid, by whose rapid evaporation a cold of -65° is obtained. Liquid SO_2 packed in sealed tins or in siphons, is now a commercial article.

Chemical.—Sulphur dioxide is neither combustible nor a supporter of combustion. Heated with H it is decomposed:



With nascent hydrogen, H_2S is formed:



Water not only dissolves the gas, but combines with it to form the true sulphurous acid, H_2SO_3 . With solutions of metallic hydroxides it forms metallic sulphites: $\text{SO}_2 + \text{KOH} = \text{KHSO}_3$; or $\text{SO}_2 + 2\text{KOH} = \text{K}_2\text{SO}_3 + \text{H}_2\text{O}$. A hydrate having the composition $\text{H}_2\text{SO}_3 \cdot 8\text{H}_2\text{O}$ has been obtained as a crystalline solid, fusible at $+4^\circ$.

Sulphur dioxide and sulphurous acid solution are powerful reducing agents, being themselves oxidized to sulphuric acid: $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$; or $\text{H}_2\text{SO}_3 + \text{O} = \text{H}_2\text{SO}_4$. It reduces nitric acid with formation of sulphuric acid and nitrogen tetroxide: $\text{SO}_2 + 2\text{HNO}_3 = \text{H}_2\text{SO}_4 + \text{N}_2\text{O}_4$. It decolorizes organic pigments, without, however, destroying the pigment, whose color may be restored by an alkali or a stronger acid. It destroys H_2S , acting, in this instance, not as a reducing but as an oxidizing agent: $4\text{SO}_2 + 3\text{H}_2\text{S} = 2\text{H}_2\text{O} + \text{H}_2\text{S}_5\text{O}_6 + \text{S}_2$. With Cl it combines directly under the influence of sunlight to form sulphuryl chloride (SO_2) Cl_2 .

Analytical Characters.—(1) Odor of burning sulphur.

(2) Paper moistened with starch paste and iodic acid solution turns blue in air containing 1 in 3,000 of SO_2 .

Sulphur Trioxide.—*Sulphuric oxide or anhydride*— SO_3 —*Molecular weight*=80—*Sp. gr.* 1.95.

Preparation.—(1) By union of SO_2 and O at 250° – 300° or in presence of spongy platinum.

(2) By heating sulphuric acid in presence of phosphoric anhydride:



(3) By heating dry sodium pyrosulphate:



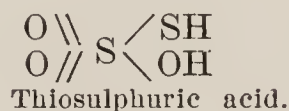
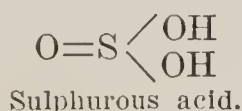
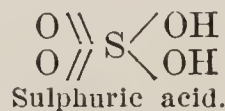
Properties.—White, silky, odorless crystals which give off white fumes in damp air. It unites with H_2O with a hissing sound, and elevation of temperature, to form sulphuric acid. When dry it does not redden litmus.

Sulphur trioxide exists in two isomeric (see isomerism) modifications, being one of the few instances of isomerism among mineral substances. The α modification, liquid at summer temperature, solidifies in colorless prisms at 16° and boils at 46° . The β isomere is a white, crystalline solid which gradually fuses and passes into the α form at about 50° .

Oxyacids of Sulphur.

H_2SO_2 Hyposulphurous acid.	$\text{H}_2\text{S}_2\text{O}_7$ Pyrosulphuric acid.
H_2SO_3 Sulphurous acid.	$\text{H}_2\text{S}_2\text{O}_6$ Dithionic acid.
H_2SO_4 Sulphuric acid.	$\text{H}_2\text{S}_3\text{O}_6$ Trithionic acid.
$\text{H}_2\text{S}_2\text{O}_8$ Persulphuric acid.	$\text{H}_2\text{S}_4\text{O}_6$ Tetrathionic acid.
$\text{H}_2\text{S}_2\text{O}_3$ Thiosulphuric acid.	$\text{H}_2\text{S}_5\text{O}_6$ Pentathionic acid.

The graphic formulæ of the chief of these acids are appended:

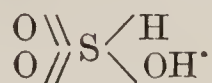


Hyposulphurous Acid— H_2SO_2 —66.—*Hydrosulphurous acid*—Is an unstable body known only in solution, obtained by the action of zinc upon solution of sulphurous acid. It is a powerful bleaching and deoxidizing agent.

Sulphurous Acid— H_2SO_3 —82.—Although sulphurous acid has not been isolated, it, in all probability, exists in the acid solution, formed when sulphur dioxide is dissolved in water: $\text{SO}_2 + \text{H}_2\text{O} = \text{SO}_3\text{H}_2$. Its salts, the sulphides, are well defined. From the existence of certain organic derivatives (see sulphonic acids) it would seem that two isomeric modifications of the acid may exist. They are distinguished as the *symmetrical*, in which the S atom is quadrivalent:



and the *unsymmetrical*, in which the S atom is hexavalent:



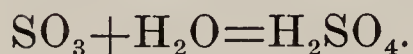
Sulphites.—The sulphites are decomposed by the stronger acids, with evolution of sulphur dioxide. Nitric acid oxidizes them to sulphates. The sulphites of the alkali metals are soluble, and are active reducing agents.

The analytical characters of the sulphites (sulphosion) are: (1) With HCl they give off SO_2 . (2) With zinc and HCl they give off H_2S . (3) With AgNO_3 they form a white ppt., soluble in excess of

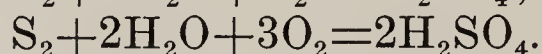
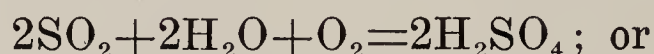
sulphite, and depositing metallic Ag when the mixture is boiled. (4) With Ba (NO₃)₂ they form a white ppt., soluble in HCl. If chlorine water is added to the solution so formed a white ppt., insoluble in acids, is produced.

Sulphuric Acid—Oil of Vitriol—Acidum sulphuricum (U. S. P.)
—H₂SO₄—98.

Preparation.—(1) By the union of sulphur trioxide and water:

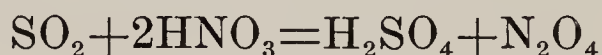


(2) By the oxidation of SO₂ or of S in the presence of water:

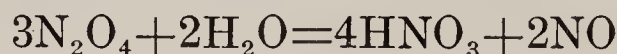


The manufacture of H₂SO₄ may be said to be the basis of all chemical industry, as there are but few processes in chemical technology into some part of which it does not enter. The method followed at present, the result of gradual improvement, may be divided into two stages: (1) the formation of a dilute acid; (2) the concentration of this product.

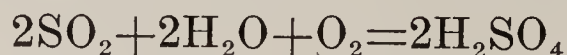
The first part is carried on in immense chambers of timber, lined with lead, and furnishes an acid having a sp. gr. of 1.55, and containing 65 per cent. of true sulphuric acid, H₂SO₄. Into these chambers SO₂, obtained by burning sulphur, or by roasting pyrites, is driven, along with a large excess of air. In the chambers it comes in contact with nitric acid, at the expense of which it is oxidized to H₂SO₄, while nitrogen tetroxide (red fumes) is formed:



Were this the only reaction, the disposal of the red fumes would present a serious difficulty and the amount of nitric acid consumed would be very great. A second reaction occurs between the red fumes and H₂O, which is injected in the form of steam, by which nitric acid and nitrogen dioxide are produced:



The nitrogen dioxide in turn combines with O to produce the tetroxide, which then regenerates a further quantity of nitric acid, and so on. This series of reactions is made to go on continuously, the nitric acid being constantly regenerated, and acting merely as a carrier of O from the air to the SO₂, in such manner that the sum of the reactions may be represented by the following equation:



The acid is allowed to collect in the chambers until it has the sp. gr. 1.55, when it is drawn off. This *chamber acid*, although used in a few industrial processes, is not yet strong enough for most purposes. It is concentrated, first, by evaporation in shallow leaden pans, until its sp. gr. reaches 1.746. At this point it begins to act

upon the lead, and is transferred to platinum stills, where the concentration is completed.

Varieties.—Sulphuric acid is met with in several conditions of concentration and purity:

(1) The *commercial oil of vitriol*, largely used in manufacturing processes, is a more or less deeply colored, oily liquid, varying in sp. gr. from 1.833 to 1.842, and in concentration from 93 per cent. to 99½ per cent. of true H_2SO_4 .

(2) *C. P. acid*=**Acidum sulphuricum** (U. S. P.), of sp. gr. 1.83 at 25°, and containing not less than 93 per cent. nor more than 95 per cent. of H_2SO_4 , is colorless and comparatively pure (see below).

(3) *Glacial sulphuric acid* is a hydrate of the composition H_2SO_4 , H_2O , sometimes called *bihydrated sulphuric acid*, which crystallizes in rhombic prisms, fusible at +8.5° when an acid of sp. gr. 1.788 is cooled to that temperature.

(4) *Diluted sulphuric acid* (U. S. P.) is a dilute acid of sp. gr. 1.067 and containing 9.5 per cent. H_2SO_4 (U. S. P.).

(5) *Aromatic sulphuric acid* (U. S. P.) contains not less than 19 per cent. and not more than 21 per cent. of H_2SO_4 .

Properties.—*Physical.*—A colorless, heavy, oily liquid; sp. gr. 1.842 at 12°; crystallizes at 10.5°; boils at 338°. It is odorless, intensely acid in taste and reaction, and highly corrosive. It is non-volatile at ordinary temperatures. Mixtures of the acid with H_2O have a lower boiling point, and lower sp. gr. as the proportion of H_2O increases.

Chemical.—At a red heat vapor of H_2SO_4 is partly dissociated into SO_3 and H_2O ; or, in the presence of platinum, into SO_2 , H_2O and O. When heated with S, C, P, Hg, Cu, or Ag, it is reduced with formation of SO_2 .

Sulphuric acid has a great tendency to absorb H_2O , the union being attended with elevation of temperature, increase of bulk, and diminution of sp. gr. of the acid, and contraction of volume of the mixture. Three parts, by weight, of acid of sp. gr. 1.842, when mixed with one part of H_2O produce an elevation of temperature to 130° and the resulting mixture occupies a volume 1-6 less than the sum of the volumes of the constituents. Strong H_2SO_4 is a good desiccator of air or gases. It should not be left exposed in uncovered vessels, lest by increase of volume it overflow. It is by virtue of its affinity for H_2O that H_2SO_4 chars or dehydrates organic substances. Sulphuric acid is a powerful dibasic acid.

The commercial acid is very impure. The colorless so-called C. P. acid may also contain: PbSO_4 , which forms a black ppt. when the dilute acid is treated with H_2S ; SO_2 , which gives off H_2S when the dilute acid is added to Zn; As, which appears as a mirror when the dilute acid is examined by Marsh's test; oxides of nitrogen, which communicate a red or pink color to pure brucine.

Sulphates.—Sulphuric acid being dibasic, there exist two sulphates of the univalent metals: HKSO_4 and K_2SO_4 , and but one sulphate of each bivalent metal: CaSO_4 . The sulphates of Ba, Ca, Sr, and Pb are insoluble, or very sparingly soluble, in H_2O . Other sulphates are soluble in H_2O , but all are insoluble in alcohol.

Analytical Characters.—Because of the dibasic character of sulphuric acid its solutions and those of its salts may contain two kinds of anion: SO_4'' in dilute solutions of the acid and in solutions of neutral sulphates, and $\text{SO}_4\text{H}'$ in concentrated solutions of the acid and in solutions of acid sulphates. In the following analytical reactions it is immaterial which anion is present if the reaction be only slightly acid, because then, as SO_4'' is removed by combination with the cations $\text{Ba}\cdot\cdot$, $\text{Pb}\cdot\cdot$, or $\text{Ca}\cdot\cdot$, the anion $\text{SO}_4\text{H}'$ is decomposed to $\text{SO}_4'' + \text{H}\cdot$; but when the solution is strongly acid a small proportion of $\text{SO}_4\text{H}'$ may remain unprecipitated.

(1) Barium chloride (or nitrate); a white ppt., insol. in dil. acids. The ppt., dried and heated with charcoal, forms BaS , which, with HCl , gives off H_2S . (2) Plumbic acetate forms a white ppt., insol. in dil. acids. (3) Calcium chloride forms a white ppt., either immediately or upon dilution with two volumes of alcohol: insol. in dil. HCl or HNO_3 .

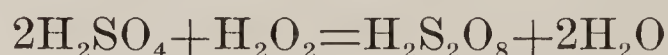
Toxicology.—Sulphuric acid is an active corrosive, and may be, if taken in sufficient quantity in a highly diluted state, a true poison. The concentrated acid causes death, either within a few hours, by corrosion and perforation of the walls of the stomach and esophagus, or, after many weeks, by starvation, due to destruction of the gastric mucous membrane and closure of the pyloric orifice of the stomach.

The treatment is the same as that for corrosion by HCl (see page 79).

Persulphuric Acid.— $\text{H}_2\text{S}_2\text{O}_8$ —194—is formed by the electrolysis of concentrated sulphuric acid:

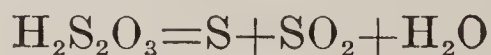


or by the action of hydrogen dioxide on sulphuric acid:



It crystallizes at 0° in long, transparent needles. The corresponding anhydride, S_2O_7 , is formed by the action of high tension electric currents in a mixture of dry SO_2 and O .

Thiosulphuric Acid.—*Hyposulphurous acid*— $\text{H}_2\text{S}_2\text{O}_3$ —114—may be considered as sulphuric acid, H_2SO_4 , in which one atom of oxygen has been replaced by one of sulphur. The acid itself has not been isolated, being decomposed, on liberation from the thiosulphates, into sulphur, water, and sulphur dioxide:



Pyrosulphuric Acid.—*Fuming sulphuric acid*—*Nordhausen oil of vitriol*— $\text{H}_2\text{S}_2\text{O}_7$ —*Molecular weight*=178—*Sp. gr.*=1.9.

Preparation.—By distilling ferrous sulphate; and purification of the product by repeated crystallizations and fusions, until a substance fusing at 35° is obtained.

Properties.—The commercial Nordhausen acid, which is a mixture of $\text{H}_2\text{S}_2\text{O}_7$ with excess of SO_3 , or of H_2SO_4 , is a brown, oily liquid, which boils below 100° , giving off SO_3 ; and is solid or liquid according to the temperature. It is used chiefly as a solvent for indigo, and in the aniline industry.

SELENIUM AND TELLURIUM.

Se—79 (International=79.2) Te—127 (International=127.5)

These are rare elements which form compounds similar to those of sulphur. Selenium is known in various allotropic modifications, and is used in some forms of electrical apparatus.

III. NITROGEN GROUP.

NITROGEN—PHOSPHORUS—ARSENIC—ANTIMONY.

The elements of this group are trivalent or quinquivalent, occasionally univalent. With hydrogen they form non-acid compounds, composed of one volume of the element in the gaseous state with three volumes of hydrogen, the union being attended with a condensation of volume of one-half.

Bismuth, frequently classed in this group, is excluded, owing to the existence of the nitrate $\text{Bi}(\text{NO}_3)_3$. The relations existing between the compounds of the elements of this group are shown in the following table:

NH_3 ,	N_2O ,	NO ,	N_2O_3 ,	NO_2 ,	N_2O_5 ,	—
PH_3 ,	—	—	P_2O_3 ,	—	P_2O_5 ,	H_3PO_2 ,
AsH_3 ,	—	—	As_2O_3 ,	—	As_2O_5 ,	—
SbH_3 ,	—	—	Sb_2O_3 ,	Sb_2O_4 ,	Sb_2O_5 ,	—
Hyd- ride.	Mon- oxide.	Di- oxide.	Tri- oxide.	Tetr- oxide.	Pent- oxide.	Hypo-ous acid.
—	—	HNO_2 ,	—	—	—	HNO_3 ,
H_3PO_3 ,	$\text{H}_4\text{P}_2\text{O}_5$,	—	H_3PO_4 ,	$\text{H}_4\text{P}_2\text{O}_7$,	—	HPO_3 ,
H_3AsO_3 ,	$\text{H}_4\text{As}_2\text{O}_5$,	HAsO_2 ,	H_3AsO_4 ,	$\text{H}_4\text{As}_2\text{O}_7$,	—	HAsO_3 ,
—	—	HSbO_2 ,	H_3SbO_4 ,	$\text{H}_4\text{Sb}_2\text{O}_7$,	—	HSbO_3 ,
-ous acid.	Pyro-ous acid.	Meta-ous acid.	-ic acid.	Pyro-ic acid.	—	Meta-ic acid.

NITROGEN.

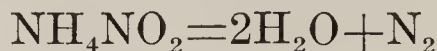
Azote—Symbol=N—Atomic weight=14 (International=14.01)—Molecular weight=28—Sp. gr.=0.9701.

Occurrence.—Free in atmospheric air and in volcanic gases. In combination in the nitrates, in ammoniacal compounds and in a great number of animal and vegetable substances.

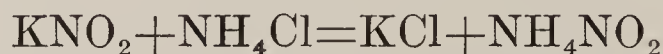
Preparation.—(1) By removal of O from atmospheric air; by burning P in air, or by passing air slowly over red-hot copper. It is contaminated with CO₂, H₂O, etc.

(2) By passing Cl through excess of ammonium hydroxide solution. If ammonia is not maintained in excess, the Cl reacts with the ammonium chloride formed, to produce the terribly explosive nitrogen chloride.

(3) By heating ammonium nitrite (NH₄)NO₂:



(4) By heating a mixture of ammonium chloride and potassium nitrite:



The ammonium nitrite then splits up as in (3).

Properties.—A colorless, odorless, tasteless, non-combustible gas; not a supporter of combustion; very sparingly soluble in water.

It is very slow to enter into combination, and most of its compounds are very prone to decomposition, which may occur explosively or slowly. Nitrogen combines directly with O under the influence of electric discharges; and with H under like conditions, and, directly, during the decomposition of nitrogenized organic substances. It combines directly with magnesium, boron, vanadium, and titanium.

Nitrogen is not poisonous, but is incapable of supporting respiration.

Atmospheric Air.—Composition.—Air is not a *chemical compound*, but a *mechanical mixture* of O and N, with smaller quantities of other gases (see page 72). Leaving out of consideration vapor of water and small quantities of other gases, except 0.03 of carbon dioxide, air consists of 20.95 O and 79.02 N (including argon), by volume; or about 23 O and 77 N, by weight; proportions which vary but very slightly at different times and places.

That air is not a compound is shown by the fact that the proportion of its constituents does not represent a relation between their atomic weights, or between any multiples thereof; as well as by the solubility of air in water. Were it a compound it would have a definite degree of solubility of its own, and the dissolved gas would have the same composition as when free. But each of its constituents dissolves in H₂O according to its own solubility, and air dissolved in H₂O at 14.1° consists of N and O, not in the proportion given above, but in the proportion of 66.76 to 33.24.

Besides these two main constituents, air contains about 4–5 thousandths of

its bulk of other substances; vapor of water, carbon dioxide, ammoniacal compounds, hydrocarbons, ozone, oxides of nitrogen, and solid particles held in suspension.

Vapor of Water.—Atmospheric moisture is either visible, as in fogs and clouds, when it is in the form of a finely divided liquid; or invisible, as vapor of water. The amount of H_2O which a given volume of air can hold, without precipitation, varies according to the temperature and pressure. It happens rarely that air is as highly charged with moisture as it is capable of being for the existing temperature. The **fraction of saturation**, or **hygrometric state**, or **relative humidity** of the atmosphere is the percentage of that quantity of vapor of water which the air could hold at the existing temperature and pressure which it actually does hold. Thus air with a humidity of 100 is saturated, and a diminution of temperature or of pressure would cause precipitation; but an increase of temperature or of pressure would cause a diminution of humidity. Ordinarily air contains from 66 to 70 per cent. of its possible amount of moisture. If the quantity is less than this, the air is dry, and causes a parched sensation, and the sense of “stuffiness” so common in furnace-heated houses. If it be greater, evaporation from the skin is impeded, and the air is oppressive if warm.

The actual amount of moisture in air is determined by passing a known volume through tubes filled with calcium chloride, whose increase in weight represents the amount of H_2O in the volume of air used. The humidity is determined by instruments called **hygrometers**, **hygroscopes** or **psychrometers**.

Carbon Dioxide.—The quantity of carbon dioxide in free air varies from 3 to 6 parts in 10,000 by volume. (See Carbon dioxide.)

For the **newer gases** in the air, see page 72.

Ammoniacal Compounds.—Carbonate, nitrate, and nitrite of ammonium occur in small quantity (0.1 to 6.0 parts per million of NH_3) in air, as products of the decomposition of nitrogenized organic substances. They are absorbed and assimilated by plants.

Nitric and Nitrous acids, usually in combination with ammonium, are produced either by the oxidation of combustible substances containing N, or by direct union of N and H_2O during discharges of atmospheric electricity. Rain-water, falling during thunder-showers, has been found to contain as much as 3.71 per million of HNO_3 .

Sulphuric and Sulphurous acids occur, in combination with NH_4 , in the air over cities, and manufacturing districts, where they are produced by the oxidation of S, existing in coal and coal-gas.

Solid particles of the most diverse nature are always present in air and become visible in a beam of sunlight. Sodium chloride is almost always present, always in the neighborhood of salt water. Air contains myriads of germs of vegetable organisms, mould, etc., which are propagated by the transportation of these germs by air-currents.

Compounds of Nitrogen and Hydrogen.—Three are known: **Ammonia**, NH_3 ; **Hydrazine**, N_2H_4 ; and **Hydrazoic acid**, N_3H ; as well as salts corresponding to two hydroxides.

Ammonia.—*Hydrogen nitride*—*Volatile alkali*— NH_3 —*Molecular weight*=17—*Sp. gr.*=0.589 A.

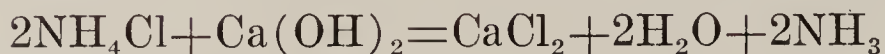
Preparation.—(1) By union of nascent H with N.

(2) By decomposition of organic matter containing N, either spontaneously or by destructive distillation.

(3) By heating solution of ammonium hydroxide:



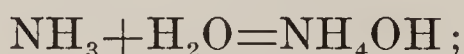
(4) By heating a mixture of ammonium chloride and slaked lime:



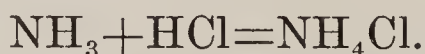
Properties.—*Physical.*—A colorless gas, having a pungent odor, and an acrid taste. It is very soluble in H_2O , 1 volume of which at 0° dissolves 1050 vols. NH_3 , and at 15° 727 vols. NH_3 . Alcohol and ether also dissolve it readily. Liquid ammonia is a colorless, mobile fluid, used in ice machines for producing artificial cold, the liquid absorbing a great amount of heat in volatilizing.

Chemical.—At a red heat ammonia is decomposed into a mixture of N and H, occupying double the volume of the original gas. It is similarly decomposed by the prolonged passage through it of discharges of electricity. It is not readily combustible, yet it burns in an atmosphere of O with a yellowish flame. Mixtures of NH_3 with O, nitrogen monoxide, or nitrogen dioxide, explode on contact with flame.

The solution of ammonia in H_2O constitutes a strongly alkaline liquid, known in the U. S. P. as **aqua ammoniæ** (*ammonia water*), which contains not less than 9.5 per cent. nor more than 10.5 per cent. NH_3 , and is possessed of strongly basic properties. It is neutralized by acids with the formation of crystalline salts, which are also formed, without liberation of hydrogen, by direct union of gaseous NH_3 with acid vapors. The ammoniacal salts and the alkaline base in aqua ammoniæ are compounds of a radical, **ammonium**, NH_4 , which forms compounds corresponding to those of potassium or sodium. The compound formed by the union of ammonia and water is **ammonium hydroxide**, NH_4OH :



and that formed by the union of hydrochloric acid and ammonia is **ammonium chloride**, NH_4Cl :



A very delicate test for ammonia is Nessler's reagent. This is made by dissolving 35 gm. of potassium iodide and 13 gm. of mercuric chloride in 800 cc. H_2O . A cold, saturated solution of mercuric chloride is then added, drop by drop, until the red precipitate formed no longer redissolves on agitation; 160 gm. of potassium hydroxide are then dissolved in the liquid, which is finally made up to 1000 cc. It gives a yellow color with a mere trace of NH_3 , and a red-brown precipitate with a larger amount.

Hydrazine—Diamide— $\text{H}_2\text{N}.\text{NH}_2$ —is known in the form of its hydroxide, corresponding to ammonium hydroxide, in the form of its salts and in numerous organic derivatives. The sulphate is produced by the action of H_2SO_4 upon

triazacetic acid, and the hydroxide by decomposition of the sulphate by caustic soda. The hydroxide is an oily liquid, intensely corrosive, capable of attacking glass. It combines with acids to form well-defined salts, and precipitates many metals from solutions of their salts. It is an active poison.

Hydrazoic Acid—Azoimide— N_3H —is a substance obtained from benzoyl-azoimide, which, although containing the same elements as ammonia, is distinctly acid in character. It is a colorless liquid, boiling at 37° , having a very pungent and unpleasant odor. It is extremely unstable and explodes with great violence. It reacts with metals, oxides, and hydroxides, as does hydrochloric acid, to form nitrides, which, like the free acid, are very explosive. It is a very active poison.

Hydroxylamine— NH_2OH —33.—The amines and amides (*q. v.*) are compounds derived from ammonia by the substitution of radicals for a part or all of its hydrogen. The substance, which is intermediate in composition between ammonia and ammonium hydroxide, may be considered as ammonia, one of whose hydrogen atoms has been replaced by the radical hydroxyl, OH . It is obtained in aqueous solution by the union of nascent hydrogen with nitrogen dioxide: $NO + H_2 = NH_2HO$; or by the action of nascent hydrogen upon nitric acid: $HNO_3 + 3H_2 = 2H_2O + NH_2HO$. Hydroxylamine has been obtained in colorless, hygroscopic crystals at 33° , by systematic rectification of the methyl alcohol solution under diminished pressure, and by distillation of the Zn double salt, $ZnCl_2 \cdot 2NH_2HO$ with aniline. Its aqueous solution, which probably contains the corresponding hydroxide, $NH_3 \cdot OH$, is strongly alkaline and behaves with regard to acids as does ammonium hydroxide solution, forming salts corresponding to those of ammonium. Thus hydroxyl-ammonium chloride, NH_4OCl , crystallizes in prisms or tables, fusible at 100° , and decomposed into HCl , H_2O and NH_4Cl at a slightly higher temperature. It is a very powerful reducing agent.

Compounds of Nitrogen with the Halogens.—Nitrogen Chloride— NCl_3 —120.5—is formed by the action of excess of Cl upon NH_3 or an ammoniacal compound. It is an oily, light-yellow liquid; sp. gr. 1.653; has been distilled at 71° . When heated to 96° , when subjected to concussion, or when brought in contact with phosphorus, alkalies or greasy matters, it is decomposed, with a violent explosion, into one volume N and three volumes Cl .

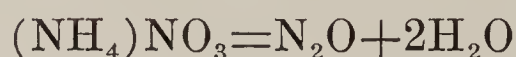
Nitrogen Bromide.— NBr_3 —254—has been obtained as a reddish-brown, syrupy liquid, very volatile, and resembling the chloride in its properties, by the action of potassium bromide upon nitrogen chloride.

Nitrogen Iodide.— NI_3 —395—When iodine is brought in contact with ammonium hydroxide solution, a dark brown or black powder, highly explosive when dried, is formed. This substance varies in composition according to the conditions under which the action occurs; sometimes the iodide alone is formed; under other circumstances it is mixed with compounds containing N , I , and H .

Oxides of Nitrogen.—Five are known, forming a regular series: N_2O , NO , N_2O_3 , N_2O_4 , N_2O_5 . Of these two, the trioxide, N_2O_3 , and pentoxide, N_2O_5 , are anhydrides.

Nitrogen Monoxide.—*Nitrogenii monoxidum* (U. S. P.)—*Nitrous oxide*—*Laughing gas*— N_2O —*Molecular weight* = 44—*Sp. gr.* = 1.527 A.

Preparation.—By heating ammonium nitrate:



To obtain a pure product there should be no ammonium chloride present (as an impurity of the nitrate), and the heat should be applied gradually and not allowed to exceed 250° , and the gas formed should be passed through wash-bottles containing sodium hydroxide and ferrous sulphate.

Properties.—*Physical.*—A colorless, odorless gas, having a sweetish taste soluble in H_2O ; more so in alcohol. Under a pressure of 30 atmospheres, at 0° , it forms a colorless, mobile liquid which, when dissolved in carbon disulphide and evaporated *in vacuo*, produces a cold of -140° .

Chemical.—It is decomposed by a red heat and by the continuous passage of electric sparks. It is not combustible, but is, after oxygen, the best supporter of combustion known.

Physiological.—Although, owing to the readiness with which N_2O is decomposed into its constituent elements, and the nature and relative proportions of these elements, it is capable of maintaining respiration longer than any gas except oxygen or air, an animal will live for a short time only in an atmosphere of pure nitrous oxide. When inhaled, diluted with air, it produces the effects first observed by Davy in 1799: first an exhilaration of spirits, frequently accompanied by laughter, and a tendency to muscular activity, the patient sometimes becoming aggressive; afterward there is complete anesthesia and loss of consciousness. It is much used, by surgeons and dentists, as an anesthetic in operations of short duration.

Nitrogen Dioxide.—*Nitric oxide*— NO —*Molecular weight*=20—*Sp. gr.*=1.039 A.

Preparation.—By the action of copper on moderately diluted nitric acid in the cold:



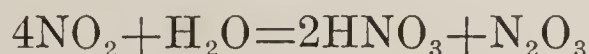
the gas being collected after displacement of air from the apparatus.

Properties.—A colorless gas, whose odor and taste are unknown; very sparingly soluble in H_2O ; more soluble in alcohol. The sp. gr. of the gas has been determined at -100° and has been found to be same as at ordinary temperature. This fixes the molecular weight at 30 and gives the formula NO , which is difficult to reconcile with the theory of valence. Were the formula doubled the constitution of this gas could be thus expressed: $\text{O}=\text{N}-\text{N}=\text{O}$. (See Nitrogen tetroxide.)

It combines with O, when mixed with that gas or with air, to form the reddish brown nitrogen tetroxide. It is absorbed by solution of ferrous sulphate, to which it communicates a dark brown or

black color. It is neither combustible nor a good supporter of combustion, although ignited C and P continue to burn in it, and the alkaline metals, when heated in it, combine with its O with incandescence.

Nitrogen Trioxide.—*Nitrous anhydride.*— N_2O_3 —76—Is prepared by the direct union of nitrogen dioxide and oxygen at low temperatures, or by decomposing liquefied nitrogen tetroxide with a small quantity of H_2O at a low temperature:



It is a dark indigo-blue liquid, which, boiling at about 0° , is partly decomposed. It solidifies at -82° .

Nitrogen Tetroxide.—*Nitrogen peroxide.*— N_2O_4 —*Molecular weight*=92.

Preparation.—(1) By mixing one volume O with two volumes NO; both dry and ice-cold.

(2) By heating perfectly dry lead nitrate, O being also produced:



(3) By dropping strong nitric acid upon a red-hot platinum surface.

Properties.—When pure and dry, it is an orange-yellow liquid at the ordinary temperature; the color being darker the higher the temperature; the gas is red-brown, but becomes colorless at about 500° . The red fumes, which are produced when nitric acid is decomposed by starch or by a metal, consist of N_2O_4 , mixed with N_2O_3 . The sp. gr. of the gas varies with the temperature and pressure. Values varying from 29.23 to 39.9 have been obtained ($\text{H}=1$). The molecular formula, NO_2 , calls for sp. gr. 23; N_2O_4 for 46. These variations are due to the fact that the gas is dissociated at comparatively low temperatures. The formula N_2O_4 has been fixed as the correct one by the method of Raoult. It dissolves in nitric acid, forming a dark yellow liquid, which is blue or green if N_2O_3 be also present. With SO_2 it combines to form a solid, crystalline compound, which is sometimes produced in the manufacture of H_2SO_4 . This substance, which forms the **lead chamber crystals**, is a substituted sulphurous acid, **nitrosulphonic acid**, $\text{NO}_2\text{SO}_2\text{OH}$ (see sulphonic acids). A small quantity of H_2O decomposes N_2O_4 into HNO_3 and N_2O_3 , which latter colors it green or blue. A larger quantity of H_2O decomposes it into HNO_3 and NO. By bases it is transformed into a mixture of nitrite and nitrate:



It is an energetic oxidant, for which it is largely used. With

certain organic substances it does not behave as an oxidant, but becomes substituted as an univalent radical; thus with benzene it forms nitro-benzene: $\text{C}_6\text{H}_5(\text{NO}_2)$.

Toxicology.—The brown fumes given off during many processes, in which nitric acid is decomposed, are dangerous to life. When in industrial processes the volume of gas formed becomes such as to be a nuisance when discharged into the air, it should be utilized in the manufacture of H_2SO_4 , or absorbed by H_2O or an alkaline solution.

An atmosphere contaminated with brown fumes is more dangerous than one containing Cl , as the presence of the latter is more immediately annoying. At first there is only coughing, and it is only two to four hours later that a difficulty in breathing is felt, death occurring in ten to fifteen hours.

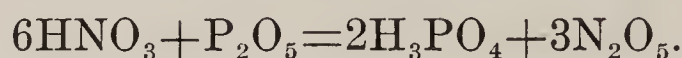
Even air containing small quantities of brown fumes, if breathed for a long time, produces chronic disease of the respiratory organs. To prevent such accidents, thorough ventilation in locations where brown fumes are liable to be formed is imperative. In cases of spilling nitric acid, safety is to be sought in retreat from the apartment until the fumes have been replaced by pure air from without.

Nitrogen Pentoxide.—*Nitric anhydride*— N_2O_5 —*Molecular weight* = 108.

Preparation.—(1) By decomposing dry silver nitrate with dry Cl in an apparatus entirely of glass:

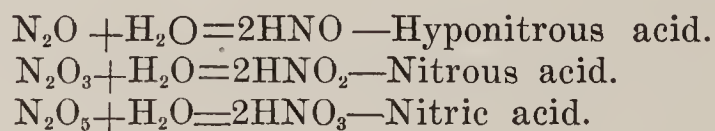


(2) By removing water from fuming nitric acid with phosphorus pentoxide:



Properties.—Prismatic crystals at temperatures above 30° . It is very unstable, being decomposed by a heat of 50° ; on contact with H_2O , with which it forms nitric acid; and even spontaneously. Most substances which combine readily with O remove that element from N_2O_5 .

Nitrogen Acids.—Three are known, either free or in combination, corresponding to the three oxides containing uneven numbers of O atoms:



Hyponitrous Acid— HNO —31—Known only in combination. Sodium hyponitrite is formed by the action of sodium upon sodium nitrate, or nitrite:



Silver hyponitrite is formed by reduction of sodium nitrate by nascent H and decomposition with silver nitrate.

Nitrous Acid—*Metanitrous acid*— HNO_2 —47—has not been isolated, although its salts, the nitrites, are well-defined compounds: $\text{M}'\text{NO}_2$ or $\text{M}''(\text{NO}_2)_2$.

The *nitrites* occur in nature, in small quantity, in natural waters, where they result from the decomposition of nitrogenous organic substances; also in saliva. They are produced by heating the corresponding nitrate, either alone or in the presence of a readily oxidizable metal, such as lead. Solutions of the nitrites are readily decomposed by the mineral acids, with evolution of brown fumes. They take up oxygen readily and are hence used as reducing agents. Solutions of potassium permanganate are instantly decolorized by nitrites. A mixture of thin starch paste and zinc iodide solution is colored blue by nitrites, which decompose the iodide, liberating the iodine. A solution of metaphenyldiamine, in the presence of free acid, is colored brown by very minute traces of a nitrite, the color being due to the formation of triamido-azobenzene (Bismark brown).

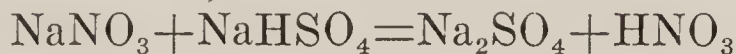
Nitric Acid. **Aquafortis**—**Acidum nitricum**—U. S. P.— HNO_3 —63.

Preparation.—(1) By the direct union of its constituent elements under the influence of electric discharges.

(2) By the decomposition of an alkaline nitrate by strong H_2SO_4 . With moderate heat a portion of the acid is liberated:



and at a higher temperature the remainder is given off:



This is the reaction used in the manufacture of HNO_3 .

Varieties.—**Commercial**—a yellowish liquid, impure, and of two degrees of concentration: **single aquafortis**; sp. gr. about 1.25=39% HNO_3 ; and **double aquafortis**; sp. gr. about 1.4=64% HNO_3 . **Fuming**—a reddish yellow liquid, more or less free from impurities; charged with oxides of nitrogen. Sp. gr. about 1.5. Used as an oxidizing agent. **C. P.**—a colorless liquid, sp. gr. 1.522, which should respond favorably to the tests given below. **Acidum nitricum**, U. S. P.—a colorless acid, of sp. gr. 1.403 at 25° =67 to 69 per cent. HNO_3 .

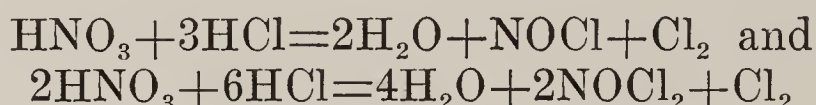
Properties.—**Physical.**—The pure acid is a colorless liquid: sp. gr. 1.522; boils at 86° ; solidifies at -40° ; gives off white fumes in damp air; and has a strong acid taste and reaction.

Chemical.—When exposed to air and light, or when strongly heated, HNO_3 is decomposed into N_2O_4 ; H_2O and O . Nitric acid is a valuable oxidant; it converts I, P, S, C, B, and Si or their lower oxides into their highest oxides; it oxidizes and destroys most organic substances, although with some it forms products of substitution.

Most of the metals dissolve in HNO_3 as nitrates, a portion of the acid being at the same time decomposed into NO and H_2O :



The chemical activity of HNO_3 is much reduced, or even almost arrested, when the intervention of nitrous acid is prevented by the presence of carbamide. The so-called **noble metals**, gold and platinum, are not dissolved by either HNO_3 or HCl , but dissolve as chlorides in a mixture of the two acids, called **aqua regia**. In this mixture the two acids mutually decompose each other according to the equations:



with formation of **nitrosyl chloride**, NOCl , and **bichloride**, NOCl_2 , and nascent Cl ; the last named combining with the metal. The **acidum nitrohydrochloricum** of the U. S. P. is a strong aqueous solution containing hydrochloric acid, nitric acid, nitrosyl chloride, and chlorine. There is also an **acidum nitrohydrochloricum dilutum** (U. S. P.), which is a diluted aqueous solution containing the same constituents as the stronger acid. Iron dissolves easily in dilute HNO_3 , but if dipped into the concentrated acid, it is rendered **passive**, and does not dissolve when subsequently brought in contact with the dilute acid. This passive condition is destroyed by a temperature of 40° (104° F.) or by contact with Pt, Ag or Cu. When HNO_3 is decomposed by zinc or iron, or in the porous cup of a Grove battery, N_2O_3 and N_2O_4 are formed, and dissolve in the acid, which is colored dark yellow, blue or green. An acid so charged is known as **nitroso-nitric acid**. Nitric acid is monobasic.

Impurities.—Oxides of nitrogen color the acid yellow: H_2SO_4 gives a white ppt. with BaCl_2 ; Cl , a white ppt. with AgNO_3 ; and Fe a red color with ammonium thiocyanate. Dilute the acid with two volumes of water before testing. Salts leave a solid residue when the acid is evaporated in platinum.

Nitrates.—The nitrates of K and Na occur in nature. Nitrates are formed by the action of HNO_3 on the metals, or on their oxides or carbonates. They have the composition $\text{M}'\text{NO}_3$, $\text{M}''(\text{NO}_3)_2$ or $\text{M}'''(\text{NO}_3)_3$, except certain basic salts, such as the sesquibasic lead-nitrate, $\text{Pb}(\text{NO}_3)_2 \cdot 2\text{PbO}$. With the exception of a few basic salts, the nitrates are all soluble in water. When heated, they fuse and act as powerful oxidants. They are decomposed by H_2SO_4 with liberation of HNO_3 .

Analytical Characters.—As the nitrates are all soluble, there is no precipitation reaction for the anion NO_3' , and recourse is had to color reactions: (1) Add an equal volume of concentrated H_2SO_4 , cool, and float on the surface of the mixture a solution of FeSO_4 .

The lower layer becomes gradually colored brown, black, or purple, beginning at the top.

(2) Boil in a test-tube a small quantity of HCl, containing enough sulphindigotic acid to communicate a blue color, add the suspected solution and boil again; the color is discharged.

(3) If acid, neutralize with KOH, evaporate to dryness, add to the residue a few drops of H₂SO₄ and a crystal of brucine (or some sulphanilic acid); a red color is produced.

(4) Add H₂SO₄ and Cu to the suspected liquid and boil, brown fumes appear (best visible by looking into the mouth of the test tube).

(5) A solution of diphenylamine in concentrated H₂SO₄ (.01 gm. in 100 cc.) is colored blue by nitric acid. A similar color is produced by other oxidizing agents.

(6) To 0.5 cc. nitrate solution add one drop aqueous solution of resorcinol (10%), and 1 drop HCl (15%), and float on the surface of 2 cc. concentrated H₂SO₄; a purple-red band.

Toxicology.—Although most of the nitrates are poisonous when taken internally in sufficiently large doses, their action seems to be due rather to the metal than to the acid radical. Nitric acid itself is one of the most powerful of corrosives.

Any animal tissue with which the concentrated acid comes in contact is rapidly disintegrated. A yellow stain, afterward turning to dirty brownish, or, if the action be prolonged, an eschar, is formed. When taken internally, its action is the same as upon the skin, but owing to the more immediately important function of the parts, is followed by more serious results (unless a large cutaneous surface is destroyed).

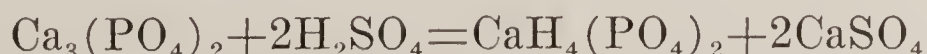
The *symptoms* following its ingestion are the same as those produced by the other mineral acids, except that all parts with which the acid has come in contact, including vomited shreds of mucous membrane, are colored yellow. The *treatment* is the same as that indicated when H₂SO₄ or HCl have been taken, *i.e.*, neutralization of the corrosive by magnesia or soap, and dilution.

PHOSPHORUS.

Symbol=P—*Atomic weight*=31 (*International*=31.04)—*Molecular weight*=124 (P₄)—*Sp. gr. of vapor*=4.2904 A.

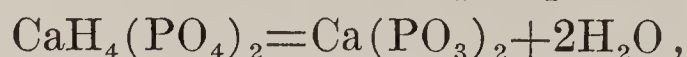
Occurrence.—Only in combination; in the mineral and vegetable worlds as phosphates of Ca, Mg, Al, Pb, K, Na. In the animal kingdom as phosphates of Ca, Mg, K and Na, and in organic combination.

Preparation.—From bone-ash in which it occurs as tricalcic phosphate. Three parts of bone-ash are digested with 2 parts of strong H₂SO₄, diluted with 20 volumes H₂O, when insoluble calcic sulphate and the soluble monocalcic phosphate, or “superphosphate,” are formed:

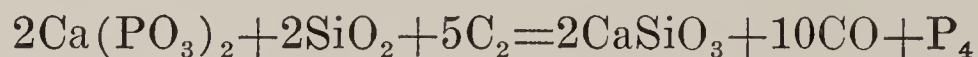


The solution of superphosphate is filtered off and evaporated, the

residue is mixed with about one-fourth its weight of powdered charcoal and sand, and the mixture heated, first to redness, finally to a white heat, in earthenware retorts, whose beaks dip under water in suitable receivers. During the first part of the heating the monocalcic phosphate is converted into metaphosphate:



which is in turn reduced by the charcoal, with formation of carbon monoxide and liberation of phosphorus, while the calcium is combined as silicate:



A direct electric process has, in great part, replaced the above industrially. A mixture of phosphate, carbon and flux is heated in a closed electric furnace provided with a condenser. The process is continuous and avoids the use of H_2SO_4 .

The crude product is purified by fusion, first under a solution of bleaching powder, next under ammoniacal H_2O , and finally under water containing a small quantity of H_2SO_4 and potassium dichromate. It is then strained through leather and cast into sticks under warm H_2O .

Properties.—*Physical.*—Phosphorus is capable of existing in four allotropic forms:

(1) *Ordinary, or yellow variety*, in which it usually occurs in commerce. This is a yellowish, translucent solid, of the consistency of wax. Below 0° it is brittle; it fuses at 44.3° ; and boils at 290° in an atmosphere not capable of acting upon it chemically. Its vapor is colorless; sp. gr. = 4.5A—65 H at 1040° . It volatilizes below its boiling point, and H_2O boiled upon it gives off steam charged with its vapor. Exposed to air it gives off white fumes and produces ozone. It is luminous in the dark. It is insoluble in H_2O ; sparingly soluble in alcohol, more soluble in ether; soluble in carbon disulphide, and in the fixed and volatile oils. It crystallizes on evaporation of its solutions in octahedræ or dodecahedræ. Sp. gr. 1.83 at 10° .

(2) *White phosphorus* is formed as a white, opaque pellicle upon the surface of the ordinary variety, when this is exposed to light under aerated H_2O . Sp. gr. 1.515 at 15° . When fused it reproduces ordinary phosphorus without loss of weight.

(3) *Black variety* is formed when ordinary phosphorus is heated to 70° and suddenly cooled.

(4) *Red variety* is produced from the ordinary by maintaining it at from 240° to 280° for two or three days, in an atmosphere of carbon dioxide; and, after cooling, washing out the unaltered yellow phosphorus with carbon disulphide. It is also formed upon the surface of the yellow variety, when it is exposed to direct sunlight.

It is a reddish, odorless, tasteless solid, which does not fume in air, nor dissolve in the solvents of the yellow variety. Sp. gr. 2.1.

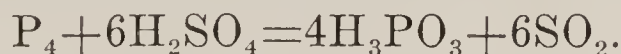
Heated to 500° with lead, in the absence of air, it dissolves in the molten metal, from which it separates on cooling in violet-black, rhombohedral crystals, of sp. gr. 2.34. If prepared at 250° it fuses below that temperature, and at 260° is transformed into the yellow variety, which distils. The crystalline product does not fuse. It is not luminous at ordinary temperatures.

Chemical.—The most prominent property of P is the readiness with which it combines with O. The yellow variety ignites and burns with a bright flame if heated in air to 60° , or if exposed in a finely-divided state to air at the ordinary temperature; with formation of P_2O_3 ; P_2O_5 ; H_3PO_3 , or H_3PO_4 , according as O is present in excess or not, and according as the air is dry or moist. The temperature of ignition of yellow P is so low that it must be preserved under boiled water. By directing a current of O upon it, P may be burned under H_2O , heated above 45° . The red variety combines with O much less readily, and may be kept in contact with air without danger.

The luminous appearance of yellow P is said to be due to the formation of ozone. It does not occur in pure O at the ordinary temperature, nor in air under pressure, nor in the absence of moisture, nor in the presence of minute quantities of carbon disulphide, oil of turpentine, alcohol, ether, naphtha, and many gases.

Yellow phosphorus burns in Cl with formation of PCl_3 or PCl_5 , according as P or Cl is present in excess. Both yellow and red varieties combine directly with Cl, Br, and I.

Phosphorus is not acted on by HCl or cold H_2SO_4 . Hot H_2SO_4 oxidizes it with formation of phosphorous acid and sulphur dioxide:



Nitric acid oxidizes it violently to phosphoric acid and nitrogen di- and tetr-oxides:



Phosphorus is a reducing agent. When immersed in cupric sulphate solution, it becomes covered with a coating of metallic copper. In silver nitrate solution it produces a black deposit of silver phosphide.

The principal uses of phosphorus are in making matches, rat paste and phosphor bronze.

Toxicology.—The red variety differs from the other allotropic forms of phosphorus in not being poisonous, probably owing to its insolubility, and in being little liable to cause injury by burning.

The burns produced by yellow phosphorus are more serious than a like destruction of cutaneous surface by other substances. A burning fragment of P adheres tenaciously to the skin, into which it burrows. One of the products of the combustion is metaphosphoric acid (*q.v.*) which, being absorbed, gives rise to true poisoning. Burns by P should be washed immediately with dilute Javelle water, liquor sodæ chlorinatæ, or solution of chloride of lime. Yellow

P should never be allowed to come in contact with the skin, except under cold water.

Yellow P is one of the most insidious of poisons. It is taken or administered usually as "ratsbane" or match-heads. The former is frequently starch paste, charged with phosphorus; the latter, in the ordinary sulphur match, a mixture of potassium chlorate, very fine sand, phosphorus, and a coloring matter. The *symptoms* in acute phosphorus-poisoning appear with greater or less rapidity, according to the dose, and the presence or absence in the stomach of substances which favor its absorption. Their appearance may be delayed for days, but as a rule they appear within a few hours. A disagreeable garlicky taste in the mouth, and heat in the stomach are first observed, the latter gradually developing into a burning pain, accompanied by vomiting of dark-colored matter, which, when shaken in the dark, is phosphorescent; low temperature and dilatation of the pupils. In some cases, death follows at this point suddenly, without the appearance of any further marked symptoms. Usually, however, the patient rallies, seems to be doing well, until, suddenly, jaundice makes its appearance, accompanied by retention of urine, and frequently delirium, followed by coma and death.

There is no known *chemical antidote* to phosphorus. The *treatment* is, therefore, limited to the removal of the unabsorbed portions of the poison by the action of an emetic, zinc or copper sulphate, or apomorphine, as expeditiously as possible, and the administration of French oil of turpentine—the older the oil the better—as a *physiological antidote*. The use of fixed oils or fats is to be avoided, as they favor the absorption of the poison, by their solvent action. The *prognosis* is very unfavorable.

Analysis.—When, after a death supposed to be caused by phosphorus, chemical evidence of the existence of the poison in the body, etc., is desired, the investigation must be made as soon after death as possible, for the reason that the element is rapidly oxidized, and the detection of the higher stages of oxidation of phosphorus is of no value as evidence of the administration of the element, because they are normal constituents of the body and of the food.

Chronic phosphorus poisoning, or *Lucifer disease*, occurs among operatives engaged in the dipping, drying, and packing of phosphorus matches. Those engaged in the manufacture of phosphorus itself are not so affected. Sickly women and children are most subject to it. The cause of the disease has been ascribed to the presence of arsenic, and to the formation of oxides of phosphorus, and of ozone. The progress of the disorder is slow, and its culminating manifestation is the destruction of one or both maxillæ by necrosis.

The frequency of the disease may be in some degree diminished by thorough ventilation of the shop, by frequent washing of the face and mouth with a weak solution of sodium carbonate, by exposing oil of turpentine in saucers in the workshops, and particularly by keeping the teeth in repair. None of these methods, however, effect a perfect prevention, which can only be attained by the substitution of the red variety of phosphorus for the yellow in this industry.

Hydrogen Phosphides.—**Gaseous hydrogen phosphide—Phosphine.**— PH_3 —34—a colorless gas, having a strong alliaceous odor, which is obtained pure by decomposing phosphonium iodide, PH_4I , with H_2O . Mixed with H and vapor of P_2H_4 , it is produced, as a spontaneously inflammable gas, by the action of hot, concentrated solution of potassium hydroxide on P, or by decomposition of calcium phosphide by H_2O . It is highly poisonous. After death, the blood is found to be of a dark violet color, and also to have, in a great measure, lost its power of absorbing oxygen.

Liquid hydrogen phosphide— P_2H_4 —66—is the substance whose vapor communicates to PH_3 its property of igniting on contact with air. It is separated by passing the spontaneously inflammable PH_3 through a bulb tube, surrounded by a freezing mixture.

It is a colorless, heavy liquid, which is decomposed by exposure to sunlight, or to a temperature of 30° .

Solid hydrogen phosphide— P_4H_2 —126—is a yellow solid, formed when P_2H_4 is decomposed by sunlight. It is not phosphorescent and only ignites at 160° .

Compounds of Phosphorus with the Halogens—**Phosphorus Trichloride**— PCl_3 —137.5—is obtained by heating P in a limited supply of Cl. It is a colorless liquid; sp. gr. 1.61; has an irritating odor; fumes in air; boils at 76° . Water decomposes it with formation of H_3PO_3 and HCl.

Phosphorus Pentachloride— PCl_5 —208.5—is formed when P is burnt in excess of Cl. It is a light yellow, crystalline solid: gives off irritating fumes; and is decomposed by H_2O .

Phosphorus Oxychloride— $POCl_3$ —153.5—is formed by the action of a limited quantity of H_2O on the pentachloride:



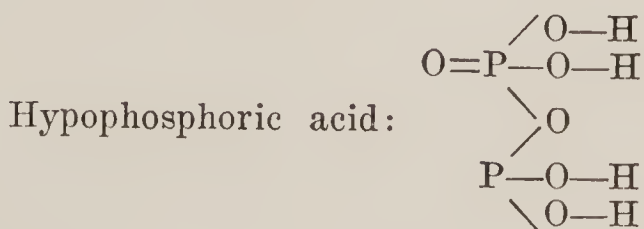
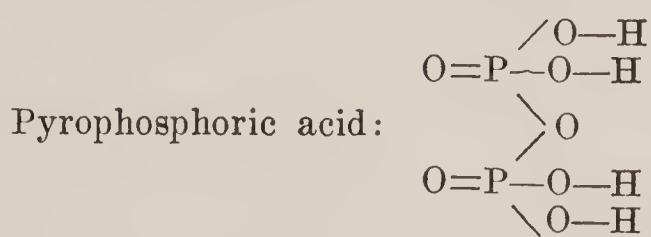
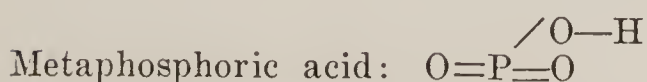
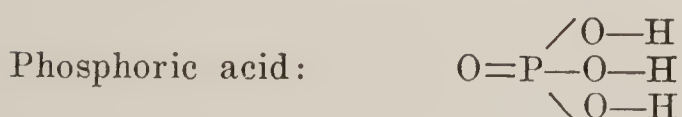
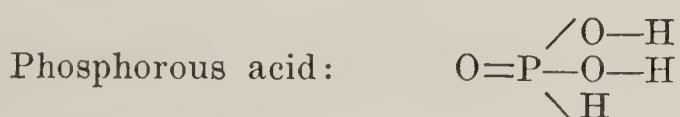
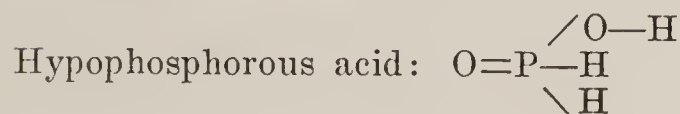
It is a colorless liquid: sp. gr. 1.07; boils at 110° , and solidifies at -10° .

Oxides of Phosphorus.—Two are known: P_2O_3 and P_2O_5 .

Phosphorus Trioxide.—*Phosphorous anhydride, Phosphorous oxide*— P_2O_3 —110—is formed when P is burned in a very limited supply of perfectly dry air, or O. It is white, flocculent solid, which, on exposure to air, ignites by the heat developed by its union with H_2O to form phosphorous acid.

Phosphorus Pentoxide.—*Phosphoric anhydride, Phosphoric oxide*— P_2O_5 —142—is formed when P is burned in an excess of dry O. It is a white, flocculent solid, which has almost as great a tendency to combine with H_2O as has P_2O_3 . It absorbs moisture rapidly, deliquescing to a highly acid liquid, containing, not phosphoric, but metaphosphoric acid. It is used as a drying agent.

Phosphorus Acids.—Six oxyacids of phosphorus are known:



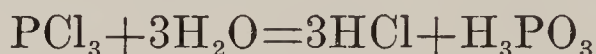
Only those H atoms which are connected with the P atoms through O atoms are basic. Hence H_3PO_2 is monobasic; H_3PO_3 is dibasic; H_3PO_4 is tribasic; $H_4P_2O_7$ is tetrabasic; HPO_2 is monobasic, and $H_4P_2O_6$ is tetrabasic.

Hypophosphorous Acid.— H_3PO_2 —66—is a crystalline solid, or, more usually, a strongly acid, colorless syrup. It is oxidized by air to a mixture of H_3PO_3 and H_3PO_4 .

The **acidum hypophosphorosum** (U. S. P.) is an aqueous solution containing not less than 30 per cent. nor more than 32 per cent. of H_3PO_2 ; and the **acidum hypophosphorosum dilutum** (U. S. P.) is an aqueous solution containing not less than 9.5 per cent. nor more than 10.5 per cent. of H_3PO_2 .

The **hypophosphites**, as well as the free acid, are powerful reducing agents.

Phosphorous Acid— H_3PO_3 —82—is formed by decomposition of phosphorus trichloride by water:

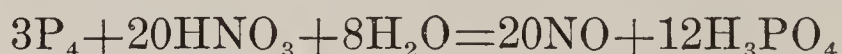


It is a highly acid syrup, is decomposed by heat, and is a strong reducing agent.

Phosphoric Acid—*Orthophosphoric acid*—**Acidum phosphoricum** (U. S. P.)— H_3PO_4 —98—does not occur free in nature, but is widely disseminated in combination, in the phosphates, in the three kingdoms of nature.

It is prepared: (1) By converting bone phosphate, $\text{Ca}_3(\text{PO}_4)_2$ into the corresponding lead or barium salt $\text{Pb}_3(\text{PO}_4)_2$ or $\text{Ba}_3(\text{PO}_4)_2$, and decomposing the former by H_2S , or the latter by H_2SO_4 .

(2) By oxidizing P by dilute HNO_3 , aided by heat:



The operation should be conducted with caution, and heat gradually applied by the sand bath. It is best to use red phosphorus.

The concentrated acid is a colorless, transparent, syrupy liquid; still containing H_2O , which it gives off on exposure over H_2SO_4 , leaving the pure acid, in transparent, deliquescent, prismatic crystals. It is decomposed by heat to form, first, pyrophosphoric acid, then metaphosphoric acid. It is tribasic.

If made from arsenical phosphorus, and commercial phosphorus is arsenical unless made by the electrolytic method (p. 20), it is contaminated with arsenic acid, whose presence may be recognized by Marsh's test (*q. v.*). The acid should not respond to the indigo and ferrous sulphate tests for HNO_3 .

The **acidum phosphoricum** (U. S. P.) contains not less than 85 per cent. nor more than 88 per cent. of H_3PO_4 ; and the **acidum phosphoricum dilutum** (U. S. P.) contains not less than 9.5 per cent. nor more than 10.5 per cent. of H_3PO_4 .

Ortho-acids are those in which the number of hydroxyls equals the valence of the acidulous elements. Thus orthophosphoric acid is $\text{P}(\text{OH})_5$; orthocarbonic acid, $\text{C}(\text{OH})_4$. Sometimes, as in the case of phosphorus, when this acid is not known, that in which the

number of hydroxyls most nearly equals the valence of the acidulous element is, improperly, called the ortho-acid.

Phosphates.—Phosphoric acid being tribasic, the phosphates have the composition $M'H_2PO_4$; M'_2HPO_4 ; M'_3PO_4 ; $M''(H_2PO_4)_2$; $M''_2(HPO_4)_2$; $M''_3(PO_4)_2$; $M''M'PO_4$; and $M'''PO_4$. The monometallic salts are all soluble and are strongly acid. Of the dimetallic salts, those of the alkali metals only are soluble and their solutions are faintly alkaline; the others are unstable, and exhibit a marked tendency to transformation into monometallic or trimetallic salts. The normal phosphates of the alkali metals are the only soluble trimetallic phosphates. Their solutions are strongly alkaline, and they are decomposed even by weak acids:



All the monometallic phosphates, except those of the alkali metals, are decomposed by ammonium hydroxide, with precipitation of the corresponding trimetallic salt.

Analytical Characters.—(1) With ammoniacal solution of silver nitrate, a yellow precipitate. (2) With solution of ammonium molybdate in HNO_3 , a yellow precipitate. (3) With magnesia mixture,* a white, crystalline precipitate, soluble in acids, insoluble in ammonium hydroxide.

Pyrophosphoric Acid— $H_4P_2O_7$ —178.—When phosphoric acid (or hydro-disodic phosphate) is maintained at 213° , two of its molecules unite, with the loss of the elements of a molecule of water: $2H_3PO_4 = H_2O + H_4P_2O_7$, to form pyrophosphoric acid.

Metaphosphoric Acid—*Glacial phosphoric acid*— HPO_3 —80—is formed by heating H_3PO_4 or $H_4P_2O_7$ to near redness: $H_3PO_4 = HPO_3 + H_2O$; or $H_4P_2O_7 = 2HPO_3 + H_2O$. It is usually obtained from bone phosphate; this is first converted into ammonium phosphate, which is then subjected to a red heat.

It is a white, glassy, transparent solid, odorless and acid in taste and reaction. Slowly deliquescent in air, it is very soluble in H_2O , although the solution takes place slowly, and is accompanied by a peculiar crackling sound. In constitution and basicity it resembles HNO_3 .

Hypophosphoric Acid— $H_4P_2O_6$ —162.—When phosphorus is exposed to moist air a strongly acid liquid is slowly formed, known as **phosphatic acid**. This is a mixture of phosphorous, phosphoric and hypophosphoric acids. The last named is separated from the others by taking advantage of the sparing solubility of its acid sodium salt; this is then converted into the lead salt, which is decomposed by H_2S ,

* Made by dissolving 11 pts. crystallized magnesium chloride and 28 pts. ammonium chloride in 130 pts. water, adding 70 pts. dilute ammonium hydroxide (sp. gr. 0.96) and filtering after two days.

and the liberated acid concentrated. It has not been crystallized. It is quite stable at the ordinary temperature, but slowly decomposes to a mixture of phosphorous and pyrophosphoric acids. It is quadribasic. It may be considered as formed by the union of a molecule of phosphoric acid and one of phosphorous acid, with loss of H_2O :
 $\text{H}_3\text{PO}_4 + \text{H}_3\text{PO}_3 = \text{H}_4\text{P}_2\text{O}_6 + \text{H}_2\text{O}$.

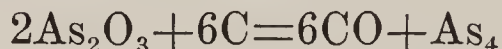
ARSENIC.

Symbol=As—*Atomic weight*=75 (*International*=74.96)—*Molecular weight*=300 (As_4)—*Sp. gr. of solid*; *crystalline*=5.75, *amorphous*=4.71; *of vapor*=10.6 A at 860° .

Occurrence.—Free in small quantity; in combination as arsenides of Fe, Co, and Ni, but most abundantly in the sulphides, orpiment and realgar, and in arsenical iron pyrites, or mispickel.

Preparation.—(1) By heating mispickel in clay cylinders, which communicate with sheet iron condensing tubes.

(2) By heating a mixture of arsenic trioxide and charcoal; and purifying the product by resublimation:



Properties.—*Physical.*—A brittle, crystalline, steel-gray solid, having a metallic luster, or a dull, black, amorphous powder. At the ordinary pressure, and without contact of air, it volatilizes without fusion at 180° ; under strong pressure it fuses at a dull red heat. Its vapor is yellowish, and has the odor of garlic. It is insoluble in H_2O , and in other liquids unless chemically altered.

Chemical.—Heated in air it is converted into the trioxide, and ignites somewhat below a red heat. In O it burns with a brilliant, bluish-white light. In dry air it is not altered, but in the presence of moisture its surface becomes tarnished by oxidation. In H_2O it is slowly oxidized, a portion of the oxide dissolving in the water. It combines readily with Cl, Br, I, and S, and with most of the metals. With H it only combines when that element is in the nascent state. Warm, concentrated H_2SO_4 is decomposed by As, with formation of SO_2 , As_2O_3 , and H_2O . Nitric acid is readily decomposed, giving up its O to the formation of arsenic acid. With hot HCl, arsenic trichloride is formed. When fused with potassium hydroxide, arsenic is oxidized, H is given off, and a mixture of potassium arsenite and arsenide remains, which by greater heat is converted into arsenic, which volatilizes, and potassium arsenate, which remains.

Elementary arsenic enters into the composition of fly poison and of shot, and is used in the manufacture of certain pigments and fireworks.

Compounds of Arsenic and Hydrogen.—Two are known: the solid As_2H_2 (?) and the gaseous AsH_3 .

Hydrogen Arsenide—Arsine—Arseniuretted hydrogen— AsH_3 —
Molecular weight=78—*Sp. gr.*=2.695 A.

Formation.—(1) By the action of dilute HCl or H_2SO_4 upon the arsenides of Zn and Sn . This is practically the same as 2, nascent hydrogen being formed by the action of the metal upon the acid.

(2) Whenever a reducible compound of arsenic is in presence of nascent hydrogen. (See Marsh test.)

(3) By the action of H_2O upon the arsenides of the alkali metals.

(4) By the action of hot solution of potassium hydroxide upon reducible compounds of As in the presence of zinc.

Properties.—*Physical.*—A colorless gas; having a strong alliaceous odor; soluble in 5 vols. of H_2O , free from air.

Chemical.—It is neutral in reaction. In contact with air and moisture its H is slowly removed by oxidation, and elementary As deposited. It is also decomposed into its elements by the passage through it of luminous electric discharges; and when subjected to a red heat. It is acted on by dry O at ordinary temperatures with the formation of a black deposit, which is at first solid hydrogen arsenide, later elementary As . A mixture of AsH_3 and O , containing 3 vols. O and 2 vols. AsH_3 , explodes when heated, forming As_2O_3 and H_2O . If the proportion of O be less, elementary As is deposited.

The gas burns with a greenish flame, from which a white cloud of arsenic trioxide arises. A cold surface, held above the flame, becomes coated with a white, crystalline deposit of the oxide. If the flame is cooled by the introduction of a cold surface into it, the H alone is oxidized, and elementary As is deposited. Chlorine decomposes the gas explosively, with formation of HCl and arsenic, or arsenic trichloride, if the Cl is in excess. In the presence of H_2O , arsenous and arsenic acids are formed. Bromine and iodine behave similarly, but with less violence.

All oxidizing agents decompose it readily; H_2O and arsenic trioxide being formed by the less active oxidants, and H_2O and arsenic acid by the more active. Solid potassium hydroxide decomposes the gas partially, and becomes coated with a dark deposit, which seems to be elementary arsenic. Solutions of the alkaline hydroxides absorb and decompose it; H is given off and an alkaline arsenite remains in the solution. Many metals, when heated in H_3As , decompose it with formation of a metallic arsenide and liberation of hydrogen. Solution of silver nitrate is reduced by it; elementary silver is deposited, and the solution contains silver arsenite.

Although H_2S and H_3As decompose each other to a great extent, with formation of arsenic trisulphide, in the presence of air, the two gases do not act upon each other at the ordinary temperature, even in the direct sunlight, either dry or in the presence of H_2O , when air is absent. Hence in making H_2S for use in toxicological analysis, materials free from As must be used; or the H_2S must be purified.

Compounds of Arsenic with the Halogens.—Arsenic Trichloride— AsCl_3 —181.5.—Obtained by distilling a mixture of As_2O_3 , H_2SO_4 , and NaCl , using a well-cooled receiver.

It is a colorless liquid, boils at 134° , fumes when exposed to the air, and volatilizes readily at temperatures below its boiling point. Its formation must be avoided in processes for the chemico-legal detection of arsenic, lest it be volatilized and lost. It is formed by the action of HCl , even when comparatively dilute, upon As_2O_3 at the temperature of the water-bath; but, if potassium chlorate be added, the trioxide is oxidized to arsenic acid, and the formation of the chloride thus prevented. Arsenic trioxide, when fused with sodium nitrate, is converted into sodium arsenate, which is not volatile. If, however, small quantities of chlorides be present, AsCl_3 is formed. It is highly poisonous.

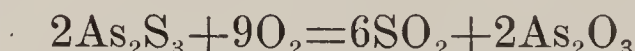
Arsenic Triiodide—Arsenii Iodidum, U. S. P.— AsI_3 —456.—Formed by adding As to a solution of I in carbon bisulphide, or by fusing together As and I in proper proportions. A brick-red solid, fusible and volatile. Soluble in a large quantity of H_2O . Decomposed by a small quantity of H_2O into HI , As_2O_3 , H_2O and a residue of AsI_3 .

Compounds of Arsenic and Oxygen.—Two are known: As_2O_3 and As_2O_5 .

Probably the gray substance formed by the action of moist air on elementary arsenic is a lower oxide.

Arsenic Trioxide—Arsenous anhydride—Arsenous oxide—White arsenic—Arsenic— As_2O_3 —198.

Preparation.—(1) By roasting the native sulphides of arsenic in a current of air:



(2) By burning arsenic in air or oxygen.

Properties.—Physical.—It occurs in three forms: *crystallized* or “*powdered*,” *vitreous*, and *porcelainous*. When freshly fused, it appears in colorless or faintly yellow, translucent, vitreous masses, having no visible crystalline structure. Shortly, however, these masses become opaque upon the surface, and present the appearance of porcelain. This change slowly progresses toward the center of the mass, which, however, remains vitreous for a long time. When arsenic trioxide is sublimed, if the vapors are condensed upon a cool surface, it is deposited in the form of brilliant octahedral crystals, which are larger and more perfect the nearer the temperature of the condensing surface is to 180° . When sublimed under slightly increased pressure, or in an atmosphere of SO_2 , right rhombic prisms occur among the octahedra. It is therefore dimorphous. The crystalline variety may be converted into the vitreous, by keeping it for some time at a temperature near its point of volatilization.

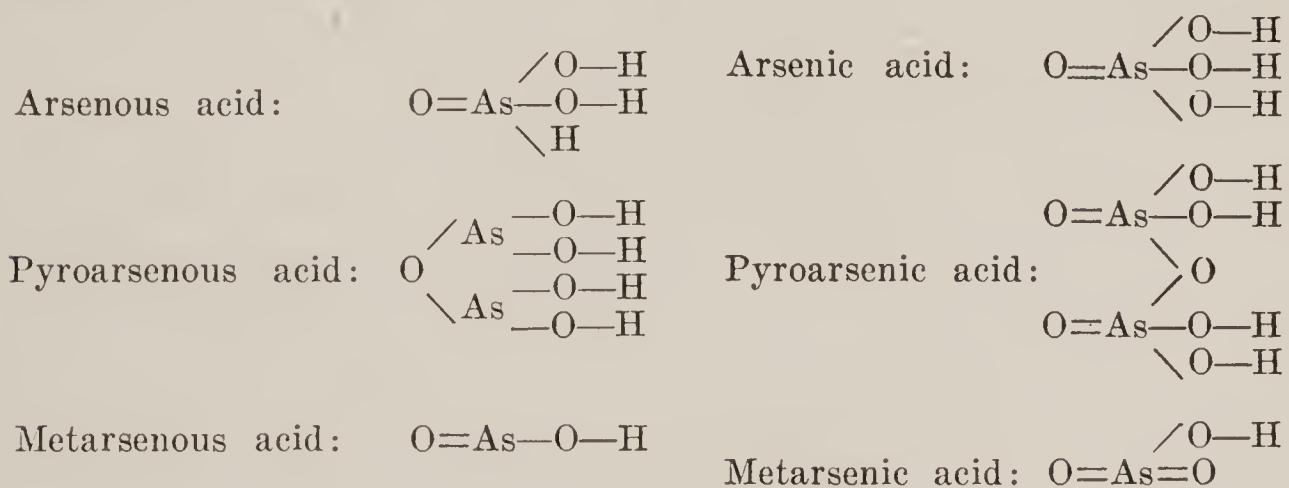
Although As_2O_3 is heavier than water, when thrown upon that liquid a large part of the crystalline powder floats, and a part of that which sinks at first subsequently rises. This is due to adhesion of air to the particles of the solid. The same phenomenon renders the

solution of As_2O_3 in water slow and irregular. The vitreous variety is more readily soluble than the crystalline. The taste of arsenic trioxide in solution is very faint, at first sweetish, afterward very slightly metallic. The solid is almost tasteless. It is odorless. In aqueous solution it has a faintly acid reaction. The sp. gr. of the vitreous variety is 3.785; that of the crystalline, 3.689.

Chemical.—Its solutions are acid in reaction, and probably contain the true arsenous acid, H_3AsO_3 . They are neutralized by bases, with formation of **arsenites**. Solutions of sodium, or potassium hydroxide, or carbonate dissolve it, with formation of the corresponding arsenite. It is readily reduced, with separation of As, when heated with hydrogen, carbon, and potassium cyanide, and at lower temperatures by more active reducing agents. Oxidizing agents, such as HNO_3 , the chlorine oxyacids, chromic acid, convert it into arsenic pentoxide or arsenic acid. Its solution, acidulated with HCl and boiled in presence of copper, deposits on the metal a gray film, composed of an alloy of Cu and As.

Arsenic Pentoxide—*Arsenic anhydride*—*Arsenic oxide*— As_2O_5 —230—is obtained by heating arsenic acid to redness. It is a white, amorphous solid, which, when exposed to the air, slowly absorbs moisture. It is fusible at a dull red heat, and at a slightly higher temperature decomposes to As_2O_3 and O_2 . It dissolves slowly in H_2O , forming arsenic acid, H_3AsO_4 .

Arsenic Acids.—The oxyacids of arsenic form a series, corresponding to that of the oxyacids of phosphorus, except that the hypoarsenous and hypoarsenic acids are unknown, and pyro- and metarsenous acids are known in their salts:



Arsenous Acid.— H_3AsO_3 —126—exists in aqueous solutions of the trioxide, although it has not been separated. Corresponding to it are important salts, called **arsenites**, which have the general formulæ $\text{HM}'_2\text{AsO}_3$, $\text{HM}''\text{AsO}_3$, $\text{H}_4\text{M}''(\text{AsO}_3)_2$. Pyro- and metarsenous acids are only known in combination.

Arsenic Acid—*Orthoarsenic acid*— H_3AsO_4 —142—is obtained by oxidizing As_2O_3 with HNO_3 in the presence of H_2O :



A similar oxidation is also effected by Cl, aqua regia, and other oxidants.

A syrupy, colorless, strongly acid solution is thus obtained, which, at 15° , becomes semi-solid, from the formation of transparent crystals, containing 1 Aq. These crystals, which are very soluble and deliquescent, lose their Aq at 100° , and form a white, pasty mass, composed of minute white, anhydrous needles. At higher temperatures it is converted into $\text{H}_4\text{As}_2\text{O}_7$, HAsO_3 , and As_2O_5 . In presence of nascent H it is decomposed into H_2O and AsH_3 . It is reducible to H_3AsO_3 by SO_2 .

Like phosphoric acid, arsenic acid is tribasic; and the arsenates resemble the phosphates in composition, and in many of their chemical and physical properties.

Metarsenic Acid— HAsO_3 —124.—At 200° – 206° $\text{H}_4\text{As}_2\text{O}_7$ gradually loses H_2O to form metarsenic acid: $\text{H}_4\text{As}_2\text{O}_7 = 2\text{HAsO}_3 + \text{H}_2\text{O}$. It forms white, pearly crystals, which dissolve readily in H_2O , with regeneration of H_3AsO_4 . It is monobasic.

Compounds of Arsenic and Sulphur.—**Arsenic Bisulphide**—*Red sulphide of arsenic*—*Realgar*—*Red orpiment*— As_2S_2 —214—occurs in nature, in translucent, ruby-red crystals. It is also prepared by heating a mixture of As_2O_3 and S. As so obtained it appears in brick-red masses.

It is fusible, insoluble in H_2O , but soluble in solutions of the alkaline sulphides, and in boiling solution of potassium hydroxide.

Arsenic Trisulphide.—*Orpiment*—*Yellow sulphide of arsenic*—*King's yellow*— As_2S_3 —246—occurs in nature in brilliant golden yellow flakes. Obtained by passing H_2S through an acid solution of As_2O_3 ; or by heating a mixture of As and S, or of As_2O_3 and S in equivalent proportions.

When formed by precipitation, it is a lemon-yellow powder, or in orange-yellow, crystalline masses, when prepared by sublimation. Almost insoluble in cold H_2O , but sufficiently soluble in hot H_2O to communicate to it a distinct yellow color. By continued boiling with H_2O it is decomposed into H_2S and As_2O_3 . Insoluble in dilute HCl ; but readily soluble in solutions of the alkaline hydroxides, carbonates, and sulphides. It volatilizes when heated.

Nitric acid oxidizes it, forming H_3AsO_4 and H_2SO_4 . A mixture of HCl and potassium chlorate has the same effect. It corresponds in constitution to As_2O_3 , and like it, may be regarded as an anhydride, for although thioarsenous acid, H_3AsS_3 , has not been separated, the thioarsenites, pyro- and meta-thioarsenites are well-characterized compounds.

Arsenic Pentasulphide— As_2S_5 —310—is formed by fusing a mixture of As_2S_3 and S in proper proportions, and, by the prolonged action of H_2S , at low temperatures, upon solutions of the arsenates.

It is a yellow, fusible solid, capable of sublimation in absence of

air. There exist well-defined thioarsenates, pyro- and meta-thioarsenates.

Action of Arsenical Compounds Upon the Animal Economy.

The poison is usually taken by the mouth, but it has also been introduced by other channels; the skin, either uninjured or abraded, the rectum, vagina, and male urethra. The forms in which it has been taken are: (1) **Elementary arsenic**, which is not poisonous so long as it remains such. In contact with water, or with the saliva, however, it is converted into an oxide, which is then dissolved, and, being capable of absorption, produces the characteristic effects of the arsenical compounds. Certain fly-papers and fly-poisons contain As, a portion of which has been oxidized by the action of air and moisture. (2) **Hydrogen arsenide**, the most actively poisonous of the inorganic compounds of arsenic, has been the cause of several accidental deaths; death has followed the inhalation of hydrogen, made from zinc and sulphuric acid contaminated with arsenic. (3) **Arsenic trioxide** is the compound most frequently used by criminals. It has been given by every channel of entrance to the circulation; and if given in large quantity, and undissolved, it may be found in the stomach after death, in the form of eight-sided crystals, more or less worn by the action of the solvents with which it has come in contact. (4) **Potassium arsenite**, the active substance in "Fowler's solution," has produced but few cases of fatal poisoning. (5) **Sodium arsenite** is sometimes used to clean metal vessels; a practice which has resulted in death or serious illness. (6) **Arsenic acid and arsenates**.—The acid itself has, so far as we know, been directly fatal to no one. But the cases of death and illness which have been put to the account of the red aniline dyes, are not due to them directly, but to arsenical residues remaining in them as the result of defective processes of manufacture. (7) **Sulphides of arsenic**.—Poisoning by these is generally due to the use of orpiment, introduced into articles of food as a coloring matter, by a combination of fraud and stupidity, in mistake for turmeric. (8) **The arsenical greens**.—Scheele's green, or cupric arsenite, and Schweinfurth green, or cupric aceto-metarsenite (the latter commonly known in the United States as **Paris green**, a name applied in Europe to one of the aniline pigments).

The arsenical pigments may also produce disastrous results by "accident;" by being incorporated in ornamental pieces of confectionery; by being used in the coloring of textile fabrics, from which they may be easily rubbed off; from their use for the destruction of insects, and by being used in the manufacture of wall-paper. Many instances of chronic or subacute arsenical poisoning have resulted from inhabiting rooms hung with paper whose whites, reds, or greens were produced by arsenical pigments. From such paper the poison is disseminated in the atmosphere of the room in two ways: either as an impalpable powder, mechanically detached from the paper and floating in the air, or by their decomposition, and the consequent diffusion of volatile arsenical compounds in the air.

The treatment in acute arsenical poisoning is the same, whatever may be the form in which the poison has been taken, if it has been taken by the mouth. The first indication is the removal of any unabsorbed poison from the alimentary canal. If vomiting has not occurred from the effects of the toxic, it should be induced by the administration of apomorphine, or zinc sulphate, or by mechanical means. When the stomach has been emptied, the chemical antidote is to be administered, with a view to the transformation, in the stomach, of any remaining arsenical compound into the insoluble, and therefore innocuous, ferrous arsenate. The U. S. P. gives an "arsenic antidote," **ferri hydroxidum cum magnesii oxido** (*ferric hydroxide with magnesium oxide*): "Mix 40 cc. of

solution of ferric sulphate with 125 cc. of water, and keep the liquid in a large, well-stoppered bottle. Rub 10 gm. magnesium oxide with cold water to a smooth and thin mixture, transfer this to a bottle capable of holding about 1000 cc., fill it with water to about three-fourths of its capacity, and keep it tightly stoppered. When the preparation is wanted for use, shake the magnesium oxide mixture until of a thin, creamy consistence, slowly add to it the diluted solution of ferric sulphate, and shake them together until a uniformly smooth mixture results." The dose is about four fluid ounces. Dialyzed iron may be given when the antidote is not obtainable.

Precautions to be taken by the Physician in cases of Suspected Poisoning.

In a case in which, from the symptoms, the physician suspects poisoning by any substance, he should himself test the urine or feces, or both, and govern his treatment and his actions toward the patient, and those surrounding the patient, by the results of his examination. Should the case terminate fatally, he should at once communicate his suspicions to the prosecuting officer, and require a post-mortem investigation, which should, if at all possible, be conducted in the presence of the chemist who is to conduct the analysis.

Cases frequently arise in which it is impossible to bring the chemist upon the ground in time for the autopsy. In such cases the physician should remember that that portion of the poison remaining in the alimentary tract (we are speaking of true poisons) is but the residue of the dose in excess of that which has been necessary to produce death; and, if the processes of elimination have been active, there may remain no trace of the poison in the alimentary canal, while it still may be detectable in the deeper-seated organs. The poison may also have been administered by another channel than the mouth, in which event it may not reach the stomach.

For these reasons it is not sufficient to send the stomach alone for analysis. The chemist should also receive the entire intestinal canal, the liver, the spleen, one or both kidneys, a piece of muscular tissue from the leg, the brain, and any urine that may remain in the bladder. The intestinal canal should be removed and sent to the chemist *without having been opened*, and with ligatures, enclosing the contents, at the two ends of the stomach and at the lower end of the intestine. The brain and alimentary canal are to be placed in separate jars, and the other viscera in another jar together; the urine in a vial by itself. All of these vessels are to be new and clean, and are to be closed by new corks, or by glass stoppers, or covers (not zinc screw-caps), which are then coated with paraffin (not sealing-wax), and so fastened with strings and seals, that it is impossible to open the vessels without cutting the strings or breaking the seals. Any vomited matters are to be preserved. If the physician fails to observe these precautions, he has probably made the breach in the evidence through which the criminal will escape, and has at the outset defeated the aim of the analysis.

Analytical Characters of the Arsenical Compounds.—ARSENOUS COMPOUNDS.—(1) H_2S , a yellow color in neutral or alkaline liquids; a yellow ppt. in acid liquids. The ppt. dissolves in solutions of the alkaline hydroxides, carbonates and sulphydrates; but is scarcely affected by HCl . Hot HNO_3 decomposes it.

(2) AgNO_3 , in the presence of a little NH_4OH , gives a yellow ppt. This test is best applied by placing the neutral arsenical solution in a porcelain capsule, adding neutral solution of AgNO_3 , and blowing upon it over the stopper of the NH_4OH bottle, moistened with that reagent.

(3) CuSO_4 under the same conditions as in (2) gives a yellowish green ppt.

(4) **Reinsch Test.**—The suspected liquid is acidulated with one-sixth its bulk of HCl . Strips of electrottype copper are immersed in the liquid, which is boiled. In the presence of an arsenous compound, a gray or bluish deposit is formed upon the Cu. A similar deposit is produced by other substances (S, Au, Pt, Bi, Sb, Hg). To complete the test the Cu is removed, washed, and dried between folds of filter paper, without removing the deposit. The copper, with its adherent film, is rolled into a cylinder, and introduced into a dry piece of Bohemian tubing, about one-fourth inch in diameter and six inches long, which is held at the angle shown in Fig. 13 and heated at the point containing the copper. If the deposit consists of arsenic, a white deposit is formed at *a*, which contains brilliant specks, and, when examined with a magnifier, is found to consist entirely of minute octahedral crystals (Fig. 14).

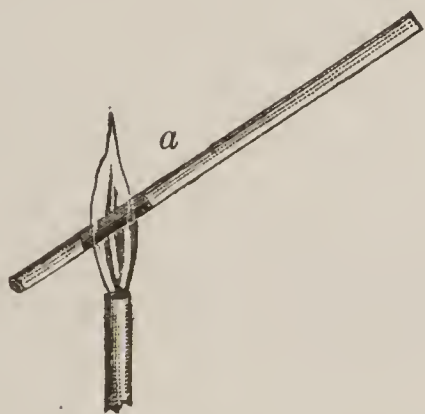


FIG. 13.

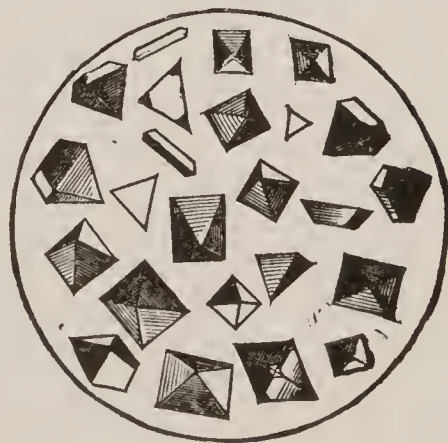


FIG. 14.

If the stain upon the copper, formed in the first part of the reaction, has been caused by S, Au, Pt, or Bi, no sublimate is produced during the subsequent heating in the glass tube, as the product of oxidation of sulphur is gaseous, Au and Pt are neither oxidized nor volatilized, and Bi is oxidized, but its oxide is not volatile. Sublimates are, however, formed from deposits caused by Sb or Hg, which differ from that produced by arsenic in the following respects: That from Sb consists of Sb_2O_3 , which is entirely, or almost entirely, amorphous, or granular, possibly containing one or two octahedral crystals, whose borders are darker than those of As_2O_3 . The sublimate from Hg consists of microscopic globules of the liquid metal. Reinsch's reaction is, therefore, a test for antimony and mercury, as well as for arsenic.

The advantages of the Reinsch test are: it may be applied in the presence of organic matter, to the urine for instance; it is easily conducted; and its positive results are not misleading, *if the test is carried to completion*. These advantages render it the most suitable method for the physician to use, *during the life of the patient*. It

should not be used *after death* by the physician, as by it copper is introduced into the substances under examination, which may subsequently interfere seriously with the analysis. The purity of the Cu and HCl must be proved by a blank testing before use. Reinsch's test is not as delicate as Marsh's, and it only reacts slowly and imperfectly when the arsenic is in the higher stage of oxidation, or in presence of oxidizing agents.

(5) **Marsh's test** is based upon the formation of AsH_3 when a reducible compound of arsenic is in presence of nascent H; and the subsequent decomposition of the arsenical gas by heat, with separation of elementary arsenic.

The apparatus used (Fig. 15) consists of a glass generating vessel, *a*, of about 150 cc. capacity, provided with a funnel-tube having a stop-cock, and a lateral outlet, either fitted in with a cork, or, better, ground in. The lateral outlet is connected with a tube, *b*, filled with fragments of calcium chloride; which in turn connects with the Bohemian glass tube *cc*, which should be about 0.5 cent. in diameter,

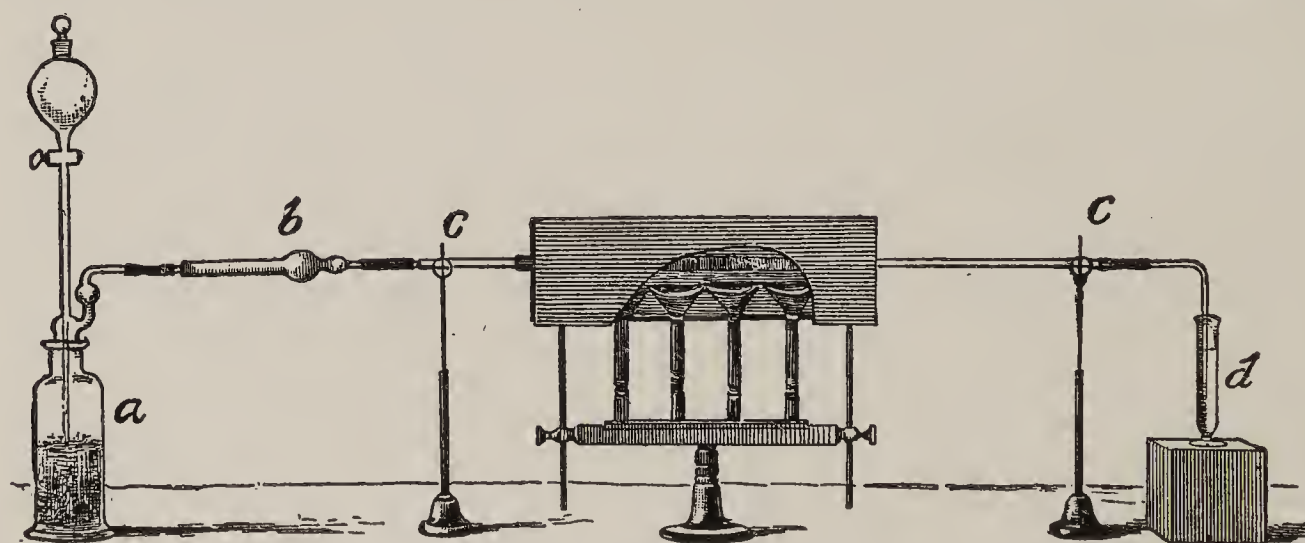


FIG. 15.

and about 80 cent. long. The tube is protected by a tube of wire gauze, within which it is adjusted in the furnace as shown in the figure. The other end of *cc* is bent downward, and dips into a solution of silver nitrate in the test-tube, *d*.

The vessel *a* is first charged with about 25 grams of an alloy of pure granulated zinc, with a small quantity of platinum. The apparatus is then connected gas-tight, and the funnel tube about half filled with H_2SO_4 , diluted with an equal bulk of H_2O , and cooled. By opening the stopcock, the acid is brought in contact with the zinc in small quantities, in such a manner that during the entire testing bubbles of gas pass through *d* at the rate of 60–80 per minute. After fifteen minutes the burner is lighted, and the heating continued, during evolution of gas from zinc and H_2SO_4 , for an hour. At the end of that time, if no stain has formed in *cc* beyond the burner, the zinc and acid may be considered to be pure, and the suspected solu-

tion, which must have been previously freed from organic matter and from tin and antimony, is introduced slowly through the funnel-tube.

If arsenic is present in the substance examined, a hair-brown or gray deposit is formed in the cool part of *cc* beyond the heated part. At the same time the contents of *d* are darkened if the amount of As present is so great that all the AsH_3 produced is not decomposed in the heated portion of *cc*.

To distinguish the stains produced by arsenical compounds from the similar ones produced by antimony the following differences are noted:

The Antimonial Stain.

The Arsenical Stain.

1. Is farther removed from the heated portion of the tube, and, if small in quantity, is double—the first hair-brown, the second steel-gray.

2. Volatilizes readily when heated in an atmosphere of hydrogen, being deposited farther along in the tube. The escaping gas has the odor of garlic.

3. When cautiously heated in a current of oxygen, brilliant, white, octahedral crystals of arsenic trioxide are deposited farther along in the tube.

4. Instantly soluble in solution of sodium hypochlorite.

5. Slowly dissolved by solution of ammonium sulphhydrate; more rapidly when warmed.

6. The solution obtained in (5) leaves, on evaporation over the water-bath, a bright yellow residue.

7. The residue obtained in (6) is soluble in aqua ammoniæ, but insoluble in hydrochloric acid.

8. Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which turns brick-red when moistened with silver nitrate solution.

9. Is not dissolved by a solution of stannous chloride.

1. Is quite near the heated portion of the tube. A second stain is also usually formed in front of the heated part of the tube.

2. Requires a much higher temperature for its volatilization; fuses before volatilizing. Escaping gas has no alliaceous odor.

3. No crystals formed by heating in oxygen, but an amorphous, white sublimate (see p. 000).

4. Insoluble in solution of sodium hypochlorite.

5. Dissolves quickly in solution of ammonium sulphhydrate.

6. The solution obtained in (5) leaves, on evaporation over the water-bath, an orange-red residue.

7. The residue obtained in (6) is insoluble in aqua ammoniæ, but soluble in hydrochloric acid.

8. Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which is not colored when moistened with silver nitrate solution.

9. Dissolves slowly in solution of stannous chloride.

The silver solution in *d* is tested for arsenous acid, by floating upon its surface a layer of diluted NH_4OH solution, which, in the presence of arsenic, produces a yellow (not brown) band, at the point of junction of the two liquids.

In place of bending the tube *c* downward, it may be bent upward and drawn out to a fine opening. If the escaping gas is then ignited,

the heating of the tube being discontinued, a white deposit of As_2O_3 may be collected on a glass surface held *above* the flame; or a brown deposit of elementary As upon a cold (porcelain) surface held *in* the flame.

In place of generating nascent hydrogen by the action of Zn on H_2SO_4 , it may be produced by the decomposition of acidulated H_2O by the battery, in a Marsh apparatus especially modified for that purpose.

In another modification of the Marsh test the AsH_3 is decomposed, not by passage through a red-hot tube, but by passing through a tube traversed by the spark from an induction coil.

ARSENIC COMPOUNDS.—(1) H_2S does not form a ppt. in neutral or alkaline solutions. In acid solutions a yellow ppt., consisting either of As_2S_3 or As_2S_5 , or a mixture of the sulphides with free S, is formed only after prolonged passage of H_2S at the ordinary temperature, more rapidly at about 70° .

(2) AgNO_3 , under the same conditions as with the arsenous compounds, produces a brick-red ppt. of silver arsenate.

(3) CuSO_4 under like circumstances produces a bluish green ppt.

Arsenic compounds behave like arsenous compounds with Marsh's test.

ANTIMONY.

Symbol=Sb (*Latin: stibium*)—*Atomic weight*=120 (*International*=120.2)—*Molecular weight*=(?)—*Sp. gr.*=6.175.

Occurrence.—Free in small quantity; principally in the trisulphide, Sb_2S_3 .

Preparation.—The native sulphide (black or crude antimony) is roasted, and then reduced by heating with charcoal.

Properties.—*Physical.*—A bluish gray, brittle solid, having a metallic luster; readily crystallizable; tasteless and odorless; volatilizes at a red heat, and may be distilled in an atmosphere of H.

Chemical.—Is not altered by dry or moist air at ordinary temperatures. When sufficiently heated in air, it burns, with formation of Sb_2O_3 , as a white, crystalline solid. It also combines directly with Cl, Br, I, S, and many metallic elements. It combines with H under the same circumstances as does As. Cold dilute H_2SO_4 does not affect it; the hot concentrated acid forms with it antimonyl sulphate $(\text{SbO})_2\text{SO}_4$ and SO_2 . Hot HCl dissolves it, when finely divided, with evolution of H. It is readily oxidized by HNO_3 , with formation of H_3SbO_4 or Sb_2O_4 . Aqua regia dissolves it as SbCl_3 , or SbCl_5 . Solutions of the alkaline hydroxides do not act on it.

The element does not form salts with the oxyacids. There are, however, compounds, formed by the substitution of the group **antimonyl** (SbO), for the basic hydrogen of those acids. (See Tartar emetic.)

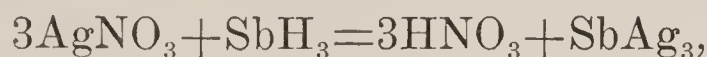
It enters into the composition of type metal, anti-friction metals, and britannia metal.

Hydrogen Antimonide—Stibine—Antimoniuretted hydrogen— SbH_3 —123.—It is produced, mixed with H_2 , when a reducible compound of Sb is in presence of nascent H . It is obtained in larger amount by decomposing an alloy of 400 parts of a 2% sodium amalgam, and 8 parts of freshly reduced, and dried Sb, by H_2O , in a current of CO_2 .

It is a colorless, odorless, combustible gas, subject to the same decompositions as AsH_3 ; from which it differs in being by no means as poisonous, and in its action upon silver nitrate solution. The arsenical gas acts upon the silver salt according to the equation:

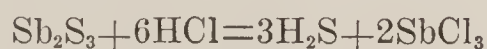


and the precipitate formed is elementary silver, while Ag_2HAsO_3 remains in the solution. In the case of SbH_3 the reaction is



all of the Sb being precipitated in the black silver antimonide.

Chlorides of Antimony.—Antimony Trichloride—Butter of antimony— SbCl_3 —226.5—is obtained by passing dry Cl over an excess of Sb_2S_3 ; by dissolving Sb_2S_3 in HCl :

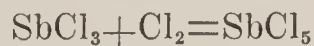


Or by distilling mixtures, either of Sb_2S_3 and mercuric chloride, or of Sb and mercuric chloride.

At low temperatures it is a solid, crystalline body; at the ordinary temperature a yellow, semi-solid mass, resembling butter; at 73.2° , it fuses to a yellow, oily liquid, which boils at 223° .

It absorbs moisture from air, and is soluble in a small quantity of H_2O ; with a larger quantity it is decomposed, with precipitation of a white powder, **powder of Algaroth**, whose composition is SbOCl if cold H_2O be used, and $\text{Sb}_4\text{O}_5\text{Cl}_2$ if the H_2O be boiling. In H_2O containing 15 per cent. or more HCl , SbCl_3 is soluble without decomposition.

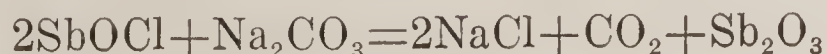
Antimony Pentachloride— SbCl_5 —297.5—is formed by the action of Cl in excess, upon Sb or SbCl_3 :



It is a fuming, colorless liquid. With a small quantity of H_2O , and evaporation over H_2SO_4 , it forms a hydrate, $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$, which appears in transparent, deliquescent crystals. With more H_2O , a crystalline oxychloride, SbOCl_3 , is formed; and with still greater quantity, a white precipitate of orthoantimonic acid, H_3SbO_4 .

Compounds of Antimony and Oxygen.—Three are known, Sb_2O_3 , Sb_2O_4 and Sb_2O_5 .

Antimony Trioxide—Antimonous anhydride—Oxide of antimony— Sb_2O_3 —288—occurs in nature; and is prepared artificially by heating Sb in air, or by decomposing the oxychloride:



It crystallizes in prisms or in octahedra, and is isodimorphous with As_2O_3 , or is an amorphous, insoluble, tasteless, odorless powder; white at ordinary temperatures, but yellow when heated. It fuses readily, and may be distilled in absence of oxygen. Heated in air, it burns like tinder, and is converted into Sb_2O_4 .

It is reduced, with separation of Sb, when heated with charcoal, or in H. It is already oxidized by HNO_3 , or potassium permanganate. It dissolves in HCl as SbCl_3 ; in Nordhausen sulphuric acid, from which solution brilliant crystalline plates of antimonyl pyrosulphate, $(\text{SbO})_2\text{S}_2\text{O}_7$, separate; and in solutions of tartaric acid, and of hydropotassic tartrate (see Tartar emetic). Boiling solutions of alkaline hydroxides convert it into antimonious acid.

Antimony Pentoxide—*Antimonic anhydride*— Sb_2O_5 —320—is obtained by heating metantimonious acid to dull redness. It is an amorphous, tasteless, odorless, pale lemon-yellow colored solid; very sparingly soluble in water and in acids. At a red heat it is decomposed into Sb_2O_4 and O.

Antimony Acids.—The normal antimonious acid, H_3SbO_3 , corresponding to H_3PO_3 , is unknown; but the series of antimonious acids: ortho, H_3SbO_4 ; pyro, $\text{H}_4\text{Sb}_2\text{O}_7$; and meta, HSbO_3 , is complete, either in the form of salts, or in that of the free acids. There also exists, in its sodium salt, a derivative of the lacking antimonious acid: **metantimonious acid**, HSbO_2 .

Sulphides of Antimony.—**Antimony Trisulphide**—*Black antimony*— Sb_2S_3 —336—is the chief ore of antimony; and is formed when H_2S is passed through a solution of tartar emetic.

The native sulphide is a steel-gray, crystalline solid; the artificial product, an orange-red, or brownish-red, amorphous powder. The **crude antimony** of commerce is in conical loaves, prepared by simple fusion of the native sulphide. It is soft, fusible, readily pulverized, and has a bright metallic luster.

Heated in air, it is decomposed into SO_2 and a brown, vitreous, more or less transparent mass, composed of varying proportions of oxide and oxysulphides, known as **crocus**, or **liver**, or **glass of antimony**. Sb_2S_3 is an anhydride, corresponding to which are salts known as **thioantimonites**, having the general formula $\text{M}'_2\text{HSbS}_3$. If an excess of Sb_2S_3 is boiled with a solution of potash or soda, a liquid is obtained, which contains an alkaline thioantimonite, and an excess of Sb_2S_3 . If this solution is filtered and allowed to cool, a brown, voluminous, amorphous precipitate separates, which consists of antimony trisulphide and trioxide, potassium or sodium sulphide, and alkaline thioantimonite in varying proportions; and is known as **Kermes mineral**.

Antimony Pentasulphide— Sb_2S_5 —400—is obtained by decomposing an alkaline thioantimonate by an acid. It is a dark orange-red, amorphous powder, readily soluble in solutions of the alkalies, and alkaline sulphides, with which it forms **thioantimonates**.

Action of Antimony Compounds on the Economy.—The compounds of antimony are poisonous, and act with greater or less energy as they are more or less soluble. The compound which is most frequently the cause of antimonial poisoning is tartar emetic (*q. v.*), which has caused death in a quantity of three grains, in divided doses, although recovery has followed the ingestion of half an ounce in several instances. Indeed, the chances of recovery seem to be better with large, than with small doses, probably owing to the more rapid and complete removal of the poison by vomiting with large doses. Antimonials have been sometimes criminally administered in small and repeated doses, the victim dying of exhaustion. In such a case an examination of the urine will reveal the cause of the trouble.

If vomiting has not occurred in cases of acute antimonial poisoning it should be provoked by apomorphine or warm water, or the stomach should be washed out. Tannin in some form (decoction of oak bark, cinchona, nutgalls, tea) should then be given, with a view to rendering any remaining poison insoluble.

Medicinal antimonials are very liable to contamination with arsenic.

Analytical Characters of Antimonial Compounds.—(1) With H_2S in acid solution: an orange-red ppt., soluble in NH_4HS and in hot HCl .

(2) A strip of bright copper, suspended in a boiling solution of an Sb compound, acidulated with HCl , is coated with a blue-gray deposit. This deposit when dried (on the copper), and heated in a tube open at both ends yields a white, *amorphous* sublimate (see Reinsch's test, p. 117).

(3) Antimonial compounds yield a deposit by Marsh's test, similar to that obtained with arsenical compounds, but differing in the particulars given above (see Marsh's test, pp. 118, 119).

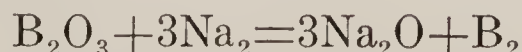
IV. BORON GROUP.

BORON.

Symbol=B—*Atomic weight*=11 (*International*=11.0)—*Molecular weight*=22.

Boron occurs in nature in the borates of Ca, Mg, and Na, principally as sodium pyroborate (borax). It constitutes a group by itself; it is trivalent in all its compounds; it forms but one oxide, which is the anhydride of a tribasic acid; and it forms no compound with H.

It is separable in two allotropic modifications. **Amorphous boron** is prepared by decomposition of the oxide, by heating with metallic potassium or sodium:



It is a greenish brown powder; sparingly soluble in H_2O ; infusible; and capable of direct union with Cl, Br, O, S, and N.

Crystallized boron is produced when the oxide, chloride or fluoride is reduced by Al. It crystallizes in quadratic prisms; more or less transparent, and varying in color from a faint yellow to deep garnet-red; very hard; sp. gr. 2.68. It burns when strongly heated in O, and readily in Cl; it also combines with N, which it is capable of removing from NH_3 at a high temperature.

Boron Trioxide.—*Boric* or *boracic anhydride*— B_2O_3 —70—is obtained by heating boric acid to redness in a platinum vessel. It is a transparent, glass-like mass, used in blowpipe analysis under the name **vitreous boric acid**.

Boric Acids.—**Boric Acid**—*Boracic acid*—*Orthoboric acid*—**Acidum boricum** (U. S. P.)— H_3BO_3 —62—occurs in nature; and is prepared by slowly decomposing a boiling, concentrated solution of borax, with an excess of H_2SO_4 , and allowing the acid to crystallize:



It forms brilliant, crystalline plates, unctuous to the touch; odorless; slightly bitter; soluble in 34 parts H_2O at 10° ; soluble in alcohol. Its solution reddens litmus, but turns turmeric paper brown. When its aqueous solution is distilled, a portion of the acid passes over.

Boric acid readily forms esters with the alcohols. When heated with ethylic alcohol, **ethyl borate** is formed, which burns with a green flame. Heated with glycerol, a soluble, neutral ester is formed, known as **boroglyceride**, and used as an antiseptic.

If H_3BO_3 be heated for some time at 80° , it loses H_2O and is converted into **metaboric acid**, HBO_2 . If maintained at 100° for several days, it loses a further quantity of H_2O , and is converted into **tetraboric** or **pyroboric acid**, $\text{H}_2\text{B}_4\text{O}_7$, whose sodium salt is borax. (See p. 154.)

V. CARBON GROUP.

CARBON—SILICON.

The elements of this group are quadrivalent. The saturated oxide of each is the anhydride of a dibasic acid. They are both combustible, and each occurs in three allotropic forms.

CARBON.

Symbol=C—*Atomic weight*=12 (*International*=12.005)—*Molecular weight*=24.

Occurrence.—Free in its three allotropic forms: The **diamond** in octahedral crystals; in alluvial sand, clay, sandstone, and conglomerate; **graphite**, in amorphous or imperfectly crystalline forms; **amorphous**, in the different varieties of anthracite and bituminous

coal, jet, etc. In combination, it is very widely distributed in the so-called organic substances.

Properties.—Diamond.—The crystals of diamond, which is almost pure carbon, are usually colorless or yellowish, but may be blue, green, pink, brown or black. It is the hardest substance known, and the one which refracts light the most strongly. Its index of refraction is 2.47 to 2.75. It is brittle; a bad conductor of heat and of electricity; sp. gr. 3.50 to 3.55. When very strongly heated in air it burns, without blackening, to carbon dioxide.

Graphite is a form of carbon almost as pure as the diamond, capable of crystallizing in hexagonal plates; sp. gr. 2.2; dark gray in color; opaque; soft enough to be scratched by the nail; and a good conductor of electricity. It is also known as **black lead** or **plumbago**. It has been obtained artificially, by allowing molten cast-iron, containing an excess of carbon, to cool slowly, and dissolving the iron in HCl. When oxidized with potassium chlorate and nitric acid it yields **graphitic acid**, $C_{11}H_4O_5$.

Amorphous carbon is met with in a great variety of forms, natural and artificial, in all of which it is black; sp. gr. 1.6–2.0; more or less porous; and a conductor of electricity.

Anthracite coal is hard and dense; it does not flame when burning; is difficult to kindle, but gives great heat with a suitable draught. It contains 80–90 per cent. of carbon. **Bituminous** coal differs from anthracite in that, when burning, it gives off gases, which produce a flame. Some varieties are quite soft, while others, such as jet, are hard enough to assume a high polish. It is usually compact in texture, and very frequently contains impressions of leaves, and other parts of plants. It contains about 75 per cent. of carbon.

Charcoal, wood charcoal, carbo ligni, (U. S. P.) is obtained by burning woody fiber, with an insufficient supply of air. It is brittle and sonorous; has the form of the wood from which it was obtained, and retains all the mineral matter present in the woody tissue. Its sp. gr. is about 1.57. It has the power of condensing within its pores odorous substances and large quantities of gases; 90 volumes of ammonia, 55 of hydrogen sulphide, 9.25 of oxygen. This property is taken advantage of in a variety of ways. Its power of absorbing odorous bodies renders it valuable as a disinfecting and filtering agent, and in the prevention of putrefaction and fermentation of certain liquids. The efficacy of charcoal as a filtering material is due also, in a great measure, to the oxidizing action of the oxygen condensed in its pores; indeed, if charcoal is boiled with dilute HCl, dried, and heated to redness, the oxidizing action of the oxygen, which it thus condenses, is very energetic.

When small strips of wood are heated to redness in a current of vapor of carbon disulphide, or of hydrocarbons, **metallic carbon** is

produced. This is very sonorous, and is a very good conductor of heat and of electricity. The filaments in incandescent electric lamps are prepared from vegetable parchment or bamboo fiber in a similar manner.

Lamp-black is obtained by incomplete combustion of some resinous or tarry substance, or natural gas, the smoke or soot from which is directed into suitable condensing chambers. It is a light amorphous powder, and contains a notable quantity of oily and tarry material, from which it may be freed by heating in a covered vessel. It is used in the manufacture of printer's ink.

Coke is the substance remaining in gas retorts, after the distillation of bituminous coal, in the manufacture of illuminating gas. It is a hard, grayish substance, usually very porous, dense, and sonorous. When iron retorts are used, a portion of the gaseous products are decomposed by contact with the hot iron surface, upon which there is then deposited a layer of very hard, compact, grayish carbon, which is a good conductor of electricity.

Animal charcoal is obtained by calcining animal matters in closed vessels. If prepared from bones it is known as **bone-black**, **carbo animalis**; if from ivory, **ivory black**. The latter is used as a pigment, the former as a decolorizing agent. Bones yield about 60 per cent. of bone-black, which contains, besides carbon, nitrogen and the phosphates and other mineral substances of the bones. It possesses in a remarkable degree the power of absorbing coloring matters. When its decolorizing power is lost by saturation with pigmentary bodies, it may be restored, although not completely, by calcination. For certain purposes purified animal charcoal, *i.e.*, freed from mineral matter, **carbo animalis purificatus**, is required, and is obtained by extracting the commercial article with HCl, and washing it thoroughly. Its decolorizing power is diminished by this treatment. Animal charcoal has the power of removing from a solution certain crystalline substances, notably the alkaloids, and a method has been suggested for separating these bodies from organic mixtures by its use.

All forms of carbon are insoluble in any known liquid.

Chemical.—All forms of C combine with O at high temperatures, with light and heat. The product of the union is carbon dioxide if the supply of air or O is sufficient; but if O is present in limited quantity, carbon monoxide is formed. The affinity of C for O renders it a valuable reducing agent. Many metallic oxides are reduced, when heated with C, and steam is decomposed when passed over red-hot C: $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$. At elevated temperatures C also combines directly with S, to form carbon disulphide. With H, carbon also combines directly, under the influence of the voltaic arc.

For Compounds of Carbon, see page 191.

SILICON.

Symbol=Si—*Atomic weight*=28 (*International*, 28.3)—*Molecular weight*=56.

Also known as **silicium**; occurs in three allotropic forms: **Amorphous silicon**, formed when silicon chloride is passed over heated K or Na, is a dark brown powder, heavier than water. When heated in air, it burns with a bright flame to the dioxide. It dissolves in potash and in hydrofluoric acid, but is not attacked by other acids. **Graphitoid silicon** is obtained by fusing potassium fluosilicate with aluminium. It forms hexagonal plates, of sp. gr. 2.49, which do not burn when heated to whiteness in O, but may be oxidized at that temperature, by a mixture of potassium chlorate and nitrate. It dissolves slowly in alkaline solutions, but not in acids. **Crystallized silicon**, corresponding to the diamond, forms crystalline needles, which are only attacked by a mixture of nitric and hydrofluoric acids.

Silicon, although closely related to C, exists in nature in comparatively few compounds; it occurs abundantly, however, as silicon dioxide and in the form of silicates.

Silicon Chloride— SiCl_4 —170—a colorless, volatile liquid, having an irritating odor; sp. gr. 1.52; boils at 59° ; formed when Si is heated to redness in Cl.

Silicon Dioxide—Silica—Silicic Oxide—Silicic anhydride—Silex— SiO_2 —60—is the most important of the compounds of silicon. It exists in nature in the different varieties of quartz, and in the rocks and sands containing that mineral, in agate, carnelian, flint, etc. Its purest native form is **rock crystal**. It may be obtained by heating a solution of sodium silicate with hydrochloric acid: $\text{Na}_2\text{SiO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{SiO}_2$. Its hydrates occur in the opal, and in solution in natural waters.

When crystallized, it is fusible with difficulty. When heated to redness with the alkaline carbonates, it forms **silicates**, which solidify to glass-like masses, on cooling. It unites with H_2O to form a number of acid hydrates. The normal hydrate, H_4SiO_4 , has not been isolated, although it probably exists in the solution obtained by adding an excess of HCl to a solution of sodium silicate. A gelatinous hydrate, soluble in water and in acids and alkalies, is obtained by adding a small quantity of HCl to a concentrated solution of sodium silicate.

Hydrofluosilicic Acid— H_2SiF_6 —144—is obtained in solution by passing the gas disengaged by gently heating a mixture of equal parts of fluorspar and pounded glass and 6 pts. H_2SO_4 through water; the disengagement tube being protected from moisture by a layer of mercury. It is used in analysis as a test for K and Na.

Silicon Carbide— SiC —is produced by the action of a powerful electric current upon a mixture of coke and aluminium silicate. It forms blue crystals, is very hard, and is used as a polishing agent under the name **Carborundum**.

VI. VANADIUM GROUP.

VANADIUM—COLUMBIUM—TANTALUM.

The elements of this group resemble those of the N group, but are usually quadrivalent.

Vanadium—V—51 (International=51.0)—a brilliant, crystalline metal; sp. gr.=5.5; which forms a series of oxides similar to those of N. No salts of V are known, but salts of vanadyl (VO) are numerous, and are used in the manufacture of aniline black.

Columbium (Niobium)—Cb. 93—(International=93.1)—a bright, steel-gray metal; sp. gr. 7.06; which burns in air to Cb_2O_5 and in Cl to CbCl_5 ; not attacked by acids.

Tantalum—Ta—181—(International=181.5)—closely resembles Cb in its chemical characters.

VII. MOLYBDENUM GROUP.

MOLYBDENUM—TUNGSTEN—OSMIUM.

The position of this group is doubtful; and it is probable that the lower oxides will be found to be basic in character, in which case the group should be transferred to the third class.

Molybdenum—Mo—96—a brittle white metal. The oxide MoO_3 , *molybdic anhydride*, combines with H_2O to form a number of acids; the ammonium salt of one of which is used as a reagent for H_3PO_4 , with which it forms a conjugate acid, *phosphomolybdic acid*, used as a reagent for the alkaloids.

Tungsten—*Wolframium*—W—184—a hard, brittle metal; sp. gr. 17.4. The oxide, WO_3 *tungstic anhydride*, is a yellow powder, forming with H_2O several acid hydrates; one of which, *metatungstic acid*, is used as a test for the alkaloids, as are also the conjugate *silico-tungstic* and *phosphotungstic acids*. Tissues impregnated with *sodium tungstate* are rendered unflammable.

Osmium—Os—191—(International=190.9)—occurs in combination with Ir in Pt ores; combustible and readily oxidized to OsO_4 . This oxide, known as *osmic acid*, forms colorless crystals, soluble in H_2O , which gives off intensely irritating vapors. It is used as a staining agent by histologists, and also in dental practice.

CLASS IV.—AMPHOTERIC ELEMENTS.

Elements whose Oxides unite with Water, some to form Bases, others to form Acids; which form Oxysalts.

The elements of this class are intermediate between the acidulous and the basylous elements, not only in the chemical relations of their oxides, but also in the products of their electrolytic dissociation. While the acidulous elements usually exist in ionized solutions in anions, which may be simple or compound, and the basylous elements exist only in cations, which are always simple, the amphoteric elements may exist in either anion or cation. When they occur in cations the ions are almost always simple, as triaurion, Au^{+++} , diferrion, Fe^{++} , plumbion, Pb^{++} etc., although rarely they are compound, as diuranylion, UO_2^{++} . When they occur in anions these are invariably compounds, as dichromanion, $\text{Cr}_2\text{O}_7^{--}$, permanganion, MnO_4^{--} , ferrocyanidion, $\text{Fe}(\text{CN})_6^{--}$, etc.

I. GOLD GROUP.

GOLD.

Symbol=Au (*Aurum*)—*Atomic weight*=197—(*International*=197.2)—*Molecular weight*=394. *Sp. gr.*=19.258—19.367.

Gold forms two series of compounds; in one, AuCl , it is univalent; in the other, AuCl_3 , trivalent. Its hydroxide, auric acid, $\text{Au}(\text{OH})_3$, corresponds to the oxide, Au_2O_3 . Its oxysalts are unstable.

It is yellow or red by reflected light, green by transmitted light, reddish purple when finely divided; not very tenacious; softer than silver; very malleable and ductile. It is not acted on by H_2O or air, at any temperature, nor by any single acid. It combines directly with Cl, Br, I, P, Sb, As and Hg. It dissolves in nitrohydrochloric acid.

Aurous Chloride— AuCl —is produced when auric chloride is heated to 185° (365° F.).

Auric Chloride—*Gold trichloride*— AuCl_3 —303.5—obtained by dissolving Au in aqua regia, evaporating at 100° , and purifying by crystallization from H_2O . Deliquescent, yellow prisms, very soluble in H_2O , alcohol and ether; readily decomposed, with separation of Au, by contact with P, or with reducing agents. Its solution, treated with the chlorides of tin, deposits a purple double stannate of Sn and Au, called "*purple of Cassius*." With alkaline chlorides it forms

double chlorides, such as **auri et sodii chloridum** (U. S. P.), which is a mixture of equal parts of gold chloride and sodium chloride.

Analytical Characters.—(1) With H_2S , from neutral or acid solution: a blackish brown ppt. in the cold; insoluble in HNO_3 and in HCl ; soluble in aqua regia, and in yellow NH_4HS . (2) With stannous chloride and a little chlorine water, a purple-red ppt., insoluble in HCl . (3) With ferrous sulphate: a brown deposit, which assumes the luster of gold when dried and burnished.

II. IRON GROUP.

CHROMIUM—MANGANESE—IRON.

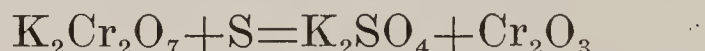
The elements of the group form two series of compounds. In one they are bivalent, as in FeCl_2 or MnSO_4 , forming the *-ous* salts; while in the other they are trivalent, as in FeCl_3 , forming the *-ic* salts. They form several oxides; of which the oxide MO_3 is an anhydride, corresponding to which are acids and salts. Most of the other oxides are basic.

CHROMIUM.

Symbol=Cr—*Atomic weight*=52—(*International*=52.0)—*Molecular weight*=104. *Sp. gr.*=6.8.

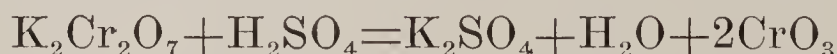
Occurs in nature principally as chrome ironstone, a double oxide of Cr and Fe. The element is separated with difficulty by reduction of its oxide by charcoal, or of its chloride by sodium. It is a hard, crystalline, almost infusible metal. Combines with O only at a red heat. It is not attacked by acids, except HCl ; is readily attacked by alkalies.

Chromic Oxide—*Chromium Sesquioxide*— Cr_2O_3 —152—obtained by heating potassium dichromate with sulphur:



It is green; insoluble in H_2O , acids and alkalies; fusible with difficulty, and not decomposed by heat; not reduced by H. At a red heat in air, it combines with alkaline hydroxides and nitrates, to form chromates. It forms two series of salts, the terms of one of which are green, those of the other violet. The alkaline hydroxides separate a bluish-green hydrate from solutions of the green salts, and a bluish violet hydrate from those of the violet salts.

Chromium Trioxide—**Chromic anhydride**—**Chromium Trioxidum** (U. S. P.)— CrO_3 —100—is formed by decomposing a solution of potassium dichromate by excess of H_2SO_4 , and crystallizing:



It crystallizes in deliquescent, crimson prisms, very soluble in H_2O

and in dilute alcohol. It is a powerful oxidant, capable of igniting strong alcohol.

The true chromic acid has not been isolated, but salts are known which correspond to three acid hydrates: H_2CrO_4 =**chromic acid**; $\text{H}_2\text{Cr}_2\text{O}_7$ =**dichromic acid**; and $\text{H}_2\text{Cr}_3\text{O}_{10}$ =**trichromic acid**.

Sulphates.—A *violet* sulphate crystallizes in octahedra, $(\text{Cr})_2(\text{SO}_4)_3 + 15\text{Aq}$, and is very soluble in H_2O . At 100° it is converted into a *green* salt, $(\text{Cr})_2(\text{SO}_4)_3 + 5\text{Aq}$, soluble in alcohol; which, at higher temperatures, is converted into the red, insoluble, anhydrous salt. Chromic sulphate forms double sulphates, containing 24 Aq, with the alkaline sulphates. (See Alums.)

Analytical Characters.—CHROMOUS SALTS.—(1) Potash: a brown ppt. (2) Ammonium hydroxide: greenish white ppt. (3) Alkaline sulphides: black ppt. (4) Sodium phosphate: blue ppt.

CHROMIC SALTS.—(1) Potash: green ppt.; an excess of precipitant forms a green solution, from which Cr_2O_3 separates on boiling. (2) Ammonium hydroxide: greenish-gray ppt. (3) Ammonium sulphhydrate: greenish ppt.

CHROMATES.—(1) H_2S in acid solution: brownish color, changing to green. (2) Ammonium sulphhydrate: greenish ppt. (3) Barium chloride: yellowish ppt. (4) Silver nitrate: brownish red ppt., soluble in HNO_3 or NH_4OH . (5) Lead acetate: yellow ppt., soluble in potash, insoluble in acetic acid.

MANGANESE.

Symbol=Mn—*Atomic weight*=55—(*International*=54.93)—*Molecular weight*=110. *Sp. gr.*=7.138—7.206.

Occurs chiefly in pyrolusite, MnO_2 , hausmanite, Mn_3O_4 , braunite, Mn_2O_3 , and manganite, Mn_2O_3 , H_2O . A hard, grayish, brittle metal; fusible with difficulty; obtained by reduction of its oxides by C at a white heat. It is not readily oxidized by cold, dry air; but is superficially oxidized when heated. It decomposes H_2O , liberating H, and dissolves in dilute acids.

Oxides.—Manganese forms six oxides, or compounds representing them: **Manganous oxide**, MnO ; **manganous manganic oxide**, Mn_3O_4 ; **manganic oxide**, Mn_2O_3 ; **manganese dioxide**, MnO_2 , and **manganese heptoxide**, Mn_2O_7 , are known free. **Manganese trioxide**, MnO_3 , has not been isolated. MnO and Mn_2O_3 are basic; Mn_3O_4 and MnO_2 are indifferent oxides; and MnO_3 and Mn_2O_7 are anhydrides, corresponding to the **manganates** and **permanganates**.

Manganese dioxide—*Black oxide of manganese*— MnO_2 —86—exists in nature as **pyrolusite**, the principal ore of manganese, in steel gray, or brownish black, imperfectly crystalline masses.

At a red heat it loses 12 per cent. of O: $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$; and

at a white heat, a further quantity of O is given off: $2\text{Mn}_2\text{O}_3 = 6\text{MnO} + \text{O}_2$. Heated with H_2SO_4 , it gives off O, and forms manganous sulphate: $2\text{MnO}_2 + 2\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$. With HCl it yields manganous chloride, H_2O and Cl: $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$. It is not acted on by HNO_3 .

The *precipitated manganese dioxide* (*Mangani dioxidum præcipitatum*) of the U. S. P. contains not less than 80 per cent. of MnO_2 .

Salts of Manganese.—Manganese forms two series of salts: **Manganous salts**, containing Mn^{II} ; and **manganic salts**, containing $(\text{Mn}_2)^{VI}$; the former are colorless or pink, and soluble in water; the latter are unstable.

Manganous Sulphate— $\text{MnSO}_4 + n\text{Aq}$ —150 + n 18—is formed by the action of H_2SO_4 on MnO_2 . Below 6° it crystallizes with 7Aq, and is isomorphous with ferrous sulphate; between 7° – 20° it forms crystals with 5 Aq, and is isomorphous with cupric sulphate; between 20° – 30° it crystallizes with 4 Aq. It is rose-colored, darker as the proportion of Aq increases, soluble in H_2O , insoluble in alcohol. With the alkaline sulphates it forms double salts, with 6 Aq.

Analytical Characters.—**MANGANOUS.**—(1) Potash: white ppt., turning brown. (2) Alkaline carbonates: white ppts. (3) Ammonium sulphhydrate: flesh-colored ppt., soluble in acids, sparingly soluble in excess of precipitant. (4) Potassium ferrocyanide: faintly reddish white ppt., in neutral solution; soluble in HCl. (5) Potassium cyanide: rose-colored ppt. forming brown solution with excess.

MANGANIC.—(1) H_2S : ppt. of sulphur. (2) Ammonium sulphhydrate: flesh-colored ppt. (3) Potassium ferrocyanide: greenish ppt. (4) Potassium ferricyanide: brown ppt. (5) Potassium cyanide: light brown ppt.

MANGANATES—are green salts, whose solutions are only stable in presence of excess of alkali, and turn brown when diluted and acidulated.

PERMANGANATES—form red solutions, which are decolorized by SO_2 , other reducing agents, and many organic substances.

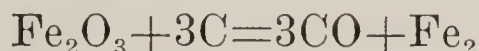
IRON.

Symbol = Fe (*Ferrum*)—*Atomic weight* = 56—(*International* = 55.84)—*Molecular weight* = 112. *Sp. gr.* = 7.25—7.9.

Occurrence.—Free, in small quantity only, in platinum ores and meteorites. As Fe_2O_3 in *red hematite* and *specular iron*; as hydrates of Fe_2O_3 in *brown hematite* and *öolitic iron*; as Fe_3O_4 in *magnetic iron*; as FeCO_3 in *spathic iron*, *clay ironstone* and *bog ore*; and as FeS_2 in *pyrites*. It is also a constituent of most soils and clays, exists in many mineral waters, and in the red blood pigment of animals.

Preparation.—In working the ores, reduction is first effected in a

blast furnace, into which alternate layers of ore, coal and limestone are fed from the top while air is forced in from below. In the lower part of the furnace CO_2 is produced, at the expense of the coal; higher up it is reduced by the incandescent fuel to CO , which, at a still higher point, reduces the ore:



The fused metal, so liberated, collects at the lowest point, under a layer of *slag*; and is drawn off to be cast as *pig iron*. This product is then purified, by burning out impurities, in the process known as *puddling*.

Pure iron is prepared by reduction of ferrous chloride, or of ferric oxide, by H at a temperature approaching redness.

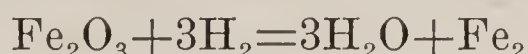
Varieties.—*Cast iron* is a brittle, white or gray, crystalline metal, consisting of Fe 89–90%; C 1–4.5%; and Si , P , S , and Mn . As *pig iron*, it is the product of the blast-furnace.

Wrought, or *bar iron*, is a fibrous, tough metal, freed in part from the impurities of cast iron, by *refining* and *puddling*.

Steel is Fe combined with a quantity of C , less than that existing in cast iron, and greater than that in bar iron. It is prepared by *cementation*; which consists in causing bar iron to combine with C ; or by the *Bessemer method*; which, as now used, consists in burning the C out of molten cast iron, to which the proper proportion of C is then added in the shape of *spiegel eisen*, an iron rich in Mn and C .

The purest forms of commercial iron are those used in piano-strings, the teeth of carding machines and electro magnets; known as *soft iron*.

Reduced iron—**Ferrum reductum** (U. S. P.)—is Fe , more or less mixed with Fe_2O_3 and Fe_3O_4 , obtained by heating Fe_2O_3 in H :



The official *ferrum reductum* contains not less than 90 per cent. of metallic iron.

Properties.—*Physical.*—Pure iron is silver white, quite soft; crystallizes in cubes or octahedra. *Wrought iron* is gray, hard, very tenacious, fibrous, quite malleable and ductile, capable of being welded, highly magnetic, but only temporarily so. *Steel* is gray, very hard and brittle if *tempered*, soft and tenacious if not, permanently magnetic.

Chemical.—Iron is not altered by dry air at the ordinary temperature. At a red heat it is oxidized. In damp air it is converted into a hydrate, *iron rust*. *Tinplate* is sheet iron, coated with tin; *galvanized iron* is coated with zinc, to preserve it from the action of damp air.

Iron unites directly with Cl , Br , I , S , N , P , As , and Sb . It dissolves in HCl as ferrous chloride, while H is liberated. Heated with strong H_2SO_4 it gives off SO_2 ; with dilute H_2SO_4 , H is given off and

ferrous sulphate formed. Dilute HNO_3 dissolves Fe, but the concentrated acid renders it *passive*, when it is not dissolved by either concentrated or dilute HNO_3 , until the passive condition is destroyed by contact with Pt, Ag or Cu, or by heating to 40° .

Compounds of Iron.—Oxides.—Three oxides of iron exist free: FeO ; Fe_2O_3 ; Fe_3O_4 .

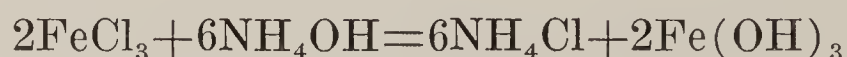
Ferrous Oxide.—*Protoxide of iron*— FeO —72—is formed by heating Fe_2O_3 in CO or CO_2 .

Ferric Oxide.—*Sesquioxide or peroxide of iron*— Fe_2O_3 —160—occurs in nature (see above), and is formed when ferrous sulphate is strongly heated, as in the manufacture of pyrosulphuric acid. It is a reddish, amorphous solid, is a weak base, and is decomposed at a white heat into O and Fe_3O_4 .

Magnetic Oxide—Ferroso-ferric oxide—Black oxide— Fe_3O_4 —232—is the **natural loadstone**, and is formed by the action of air, or steam, upon iron at high temperatures. It is probably a compound of ferrous and ferric oxides (FeO , Fe_2O_3), as acids produce with it mixtures of ferrous and ferric salts.

Hydroxides—Ferrous.—When a solution of a ferrous salt is decomposed by an alkaline hydroxide, a greenish-white hydroxide, $\text{Fe}(\text{OH})_2$ is deposited; which rapidly absorbs O from the air, with formation of ferric hydroxide.

Ferric.—When an alkali is added to a solution of a ferric salt, a brown, gelatinous precipitate is formed, which is **ferric hydroxide**, $\text{Fe}(\text{OH})_3$:



It is not formed in the presence of fixed organic acids or of sugar in sufficient quantity. If preserved under H_2O , it is partly oxidized, forming an oxyhydrate which is incapable of forming ferrous arsenate with As_2O_3 . (See p. 115.)

If recently precipitated ferric hydroxide is dissolved in solution of ferric chloride or acetate, and subjected to dialysis, almost all the acid passes out, leaving in the dialyzer a dark red solution, which probably contains this colloid hydrate, and which is instantly coagulated by a trace of H_2SO_4 , by alkalies, many salts, and by heat; **dialyzed iron**.

Sulphides.—Ferrous Sulphide—Protosulphide of iron— FeS —88—is formed:

(1) By heating a mixture of finely-divided Fe and S to redness; (2) by pressing roll-sulphur on white-hot iron; (3) in a hydrated condition, FeS , H_2O , by treating a solution of a ferrous salt with an alkaline sulphydrate.

The dry sulphide is a brownish, brittle, magnetic solid, insoluble in H_2O , soluble in acids with evolution of H_2S . The hydrate is a black powder, which absorbs O from the air, turning yellow, by

formation of Fe_2O_3 , and liberation of S. It occurs in the feces of persons taking chalybeate waters or preparations of iron.

Ferric Sulphide—Sesquisulphide— Fe_2S_3 —208—occurs in nature in *copper pyrites*, and is formed when the disulphide is heated to redness.

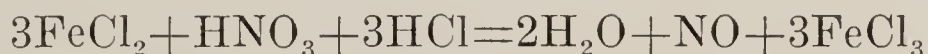
Ferric Disulphide— FeS_2 —120—occurs in the *white* and *yellow Martial pyrites*, used in the manufacture of H_2SO_4 . When heated in air, it is decomposed into SO_2 and *magnetic pyrites*:



Chlorides. — Ferrous Chloride—Protochloride— FeCl_2 —127—is produced: (1) by passing dry HCl over red-hot Fe ; (2) by heating ferric chloride in H .

The anhydrous compound is a yellow, crystalline, volatile, and very soluble solid. The hydrated is in greenish, oblique rhombic prisms, deliquescent and very soluble in H_2O and alcohol. When heated in air it is converted into ferric chloride, and an oxy-chloride.

Ferric Chloride—Sesquichloride—Perchloride—Ferri chloridum (U. S. P.)— FeCl_3 is produced by heating FeCl_2 in aqua regia:



(2) By dissolving ferric hydroxide in HCl ; (3) by the action of Cl or of HNO_3 on solution of ferrous chloride.

The anhydrous compound forms reddish-violet, crystalline plates, very deliquescent. The hydrates form yellow, nodular, imperfectly crystalline masses, or rhombic plates, very soluble in H_2O , soluble in alcohol and ether. In solution, it is converted into FeCl_2 by reducing agents. The **Liquor ferri chloridi** (U. S. P.) is an aqueous solution of this compound, containing excess of acid. The **Tincture ferri chloridi** (U. S. P.) is the solution, diluted with alcohol.

Sulphates.—Ferrous Sulphate—Protosulphate—Green vitriol—Copperas—Ferri sulphas (U. S. P.)— $\text{FeSO}_4 + 7\text{Aq}$ —152+126—is formed: (1) by oxidation of the sulphide, Fe_3S_4 , formed in the manufacture of H_2SO_4 ; (2) by dissolving Fe in dilute H_2SO_4 .

It forms green, efflorescent, oblique rhombic prisms, quite soluble in H_2O , insoluble in alcohol. It loses 6 Aq at 100° (**Ferri sulphas exsiccatus**, U. S. P.); and the last Aq at about 300° . At a red heat it is decomposed into Fe_2O_3 ; SO_2 and SO_3 . By exposure to air it is gradually converted into a basic ferric sulphate $\text{Fe}_2(\text{SO}_4)_3, 5\text{Fe}_2\text{O}_3$.

Ferric Sulphates are quite numerous, and are formed by oxidations of ferrous sulphate under different conditions. The normal sulphate, $(\text{Fe}_2)(\text{SO}_4)_3$, is formed by treating solution of FeSO_4 with HNO_3 , and evaporating, after addition of one molecule of H_2SO_4 for each two molecules of FeSO_4 . The **Liquor ferri tersulphatis** (U. S. P.), contains this salt. It is a yellowish white, amorphous solid.

Of the many **basic ferric sulphates**, the only one of medical interest is **Monsel's salt**, $5\text{Fe}_2(\text{SO}_4)_3 + 4\text{Fe}_2\text{O}_3$, which exists in the **Liquor ferri subsulphatis** (U. S. P.). Its solution is decolorized, and forms a white deposit with excess of H_2SO_4 .

Phosphates.—**Triferrous Phosphate**— $\text{Fe}_3(\text{PO}_4)_2$ —358.—A white précipitate, formed by adding disodic phosphate to a solution of a ferrous salt, in presence of sodium acetate. By exposure to air it turns blue; a part being converted into ferric phosphate. It is insoluble in H_2O ; sparingly soluble in H_2O containing carbonic or acetic acid.

It is probably this phosphate, capable of turning blue, which sometimes occurs in the lungs in phthisis, in blue pus, and in long-buried bones.

Ferric Phosphate— FePO_4 —151—is produced by the action of an alkaline phosphate on ferric chloride. It is soluble in HCl , HNO_3 , citric and tartaric acids, insoluble in phosphoric acid and in solution of disodic phosphate. The **ferri phosphas** (U. S. P.) is a compound, or mixture of this salt with disodic citrate, which is soluble in water.

There exist quite a number of basic ferric phosphates.

Acetates.—**Ferrous Acetate**— $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ —174—is formed by decomposition of ferrous sulphate by calcium acetate, in soluble, silky needles.

Ferric Acetates.—The *normal salt* $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$, is obtained by adding slight excess of ferric sulphate to lead acetate, and decanting after twenty-four hours. It is dark-red, uncrystallizable, very soluble in alcohol, and in H_2O . If its solution be heated it darkens suddenly, gives off acetic acid, and contains a basic acetate. When boiled, it loses all its acetic acid, and deposits ferric hydrate. When heated in closed vessels to 100° , and treated with a trace of mineral acid, it deposits the modified ferric hydrate.

Ferrous Carbonate— FeCO_3 —*Spathic iron*—116—occurs as an ore of iron, and is obtained, in a hydrated form, by adding an alkaline carbonate to a ferrous salt. It is a greenish, amorphous powder, which on exposure to air turns red by formation of ferric hydrate; a change which is retarded by the presence of sugar, hence the addition of that substance in the **ferri carbonas saccharatus** (U. S. P.). It is insoluble in pure H_2O , but soluble in H_2O containing carbonic acid, probably as **ferrous bicarbonate**, $\text{H}_2\text{Fe}(\text{CO}_3)_2$, in which form it occurs in chalybeate waters.

Citrates.—**Ferric Citrate**— $\text{Fe}_2(\text{C}_6\text{H}_5\text{O}_7)_2 + 6\text{Aq}$ —490+108—is in garnet-colored scales, obtained by dissolving ferric hydrate in solution of citric acid, and evaporating the solution at about 60° . It loses 3Aq at 120° , and the remainder at 150° . If a small quantity of ammonium hydroxide is added, before the evaporation, the product consists of the **modified citrate**—**ferri et ammonii citras** (U. S. P.), which only reacts with potassium ferrocyanide after addition of HCl .

The various citrates of iron and alkaloids are not definite compounds.

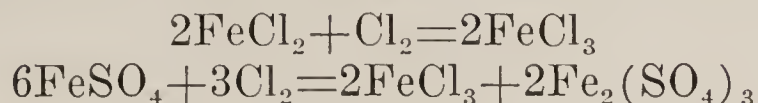
Ferric Ferrocyanide—**Prussian blue**— $(\text{Fe}_2)_2(\text{FeC}_6\text{N}_6)_3 + 18\text{Aq}$ —860+324—is a dark-blue précipitate, formed when potassium ferrocyanide is added to a

ferric salt. It is insoluble in H_2O , alcohol and dilute acids; soluble in oxalic acid solution (blue ink). Alkalies turn it brown.

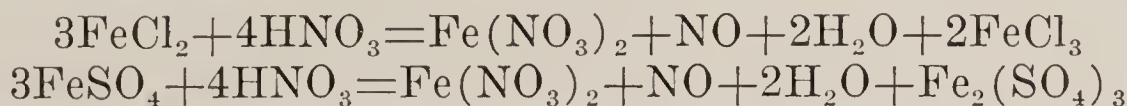
Ferrous Ferricyanide—Turnbull's blue— $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2 + n\text{Aq} - 592 + n18$ —is a dark blue substance produced by the action of potassium ferricyanide on ferrous salts. Heated in air it is converted into Prussian blue and ferric oxide.

General methods of oxidizing a ferrous salt to the ferric state.

(1) By passing chlorine gas through a solution of the ferrous salt:

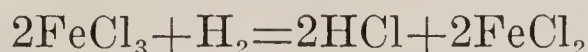


(2) By heating a solution of the ferrous salt with nitric acid:

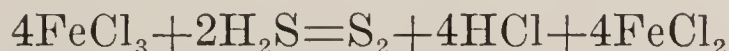


General methods of reducing a ferric salt to the ferrous state.

(1) By adding zinc and hydrochloric acid to a solution of a ferric salt; the nascent hydrogen which is liberated will effect the reduction:



(2) By passing sulphuretted hydrogen through a solution of a ferric salt:



Analytical Characters.—**FERROUS**—Are acid; colorless when anhydrous, pale green when hydrated; oxidized by air to basic ferric compounds. (1) Potash: greenish white ppt.; insoluble in excess; changing to green or brown in air. (2) Ammonium hydroxide; greenish ppt.; soluble in excess; not formed in presence of ammoniacal salts. (3) Ammonium sulphhydrate: black ppt.; insoluble in excess; soluble in acids. (4) Potassium ferrocyanide (in absence of ferric salts): white ppt.; turning blue in air. (5) Potassium ferricyanide: blue ppt.; soluble in KOH ; insoluble in HCl .

FERRIC—Are acid, and yellow or brown. (1) Potash, or ammonium hydroxide: voluminous, red-brown ppt.; insoluble in excess. (2) Hydrogen sulphide, in acid solution: milky ppt. of sulphur; ferric reduced to ferrous compound. (3) Ammonium sulphhydrate: black ppt.; insoluble in excess; soluble in acids. (4) Potassium ferrocyanide: dark blue ppt.; insoluble in HCl ; soluble in KOH . (5) Potassium thiocyanate: dark-red color; prevented by tartaric or citric acid; discharged by mercuric chloride. (6) Tannin: blue-black color.

III. URANIUM GROUP.

URANIUM.

Symbol=U—*Atomic weight*=238—(*International*=238.3).—*Sp. gr.*=18.4.

This element is usually classed with Fe and Cr, or with Ni and Co. It does not, however, form compounds resembling the ferric; it

forms a series of well-defined *uranates*, and a series of compounds of the radical *uranyl* (UO)'. Uranium nitrate, **Uranii nitras**, (U. S. P.) contains not less than 98 per cent. of $\text{UO}_2(\text{NO}_3)_2 + 6\text{Aq.}$ (**uranyl nitrate**). Standard solutions of its acetate or nitrate are used for the quantitative determination of H_3PO_4 .

IV. LEAD GROUP.

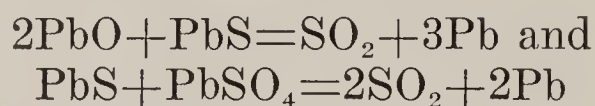
LEAD.

Symbol=Pb (*Plumbum*)—*Atomic weight*=207—(*International*=207.20)—*Molecular weight*=414.—*Sp. gr.*=11.445.

Lead is usually classed with Cd, Bi, or Cu and Hg. It differs, however, from Bi in being bivalent or quadrivalent, but not trivalent, and in forming no compounds resembling those of bismuthyl (BiO); from Cd, in the nature of its O compounds; and from Cu and Hg in forming no compounds similar to the mercurous and cuprous salts. Indeed, the nature of the Pb compounds is such that the element is best classed in a group by itself, which finds a place in this class by virtue of the existence of potassium plumbate.

Occurrence.—Its most abundant ore is **galena**, PbS . It also occurs in **white lead ore**, PbCO_3 , in **anglesite**, PbSO_4 , and in **horn lead**, PbCl_2 .

Preparation.—Galena is first roasted with a little lime. The mixture of PbO , PbS , and PbSO_4 obtained is strongly heated in a reverberatory furnace, when SO_2 is driven off:



The impure *work lead*, so formed, is purified by fusion in air, and removal of the film of oxides of Sn and Sb. If the ore is rich in Ag, that metal is extracted, by taking advantage of the greater fusibility of an alloy of Pb and Ag, than of Pb alone; and subsequent oxidation of the remaining Pb.

Properties.—*Physical.*—It is a bluish white metal; brilliant upon freshly cut surfaces; very soft and pliable; not very malleable or ductile; crystallizes in octahedra; a poor conductor of electricity; a better conductor of heat. When expanded by heat it does not, on cooling, return to its original volume.

Chemical.—When exposed to air it is oxidized, more readily and completely at high temperatures. The action of H_2O on Pb varies with the conditions. (See p. 67.) Pure unaerated H_2O has no action upon it. By the combined action of air and moisture Pb is oxidized, and the oxide dissolved in the H_2O , leaving a metallic surface for the continuance of the action. The solvent action of H_2O upon Pb is

increased, owing to the formation of basic salts, by the presence of nitrogenized organic substances, nitrates, nitrites, and chlorides. On the other hand, carbonates, sulphates, and phosphates, by their tendency to form insoluble coatings, diminish the corroding action of H_2O . Carbonic acid in small quantity, especially in presence of carbonates, tends to preserve Pb from solution, while H_2O highly charged with it (soda water) dissolves the metal readily. Lead is dissolved, as a nitrate, by HNO_3 . H_2SO_4 , when cold and moderately concentrated, does not affect it; but, when heated, dissolves it the more readily as the acid is more concentrated. It is attacked by HCl of sp. gr. 1.12, especially if heated. Acetic acid dissolves it as acetate, or, in the presence of CO_2 , converts it into white lead.

Oxides.—**Lead Monoxide**—**Massicot**—**Litharge**—**Plumbi oxidum** (U. S. P.)— PbO —223—is prepared by heating Pb, or its carbonate, or nitrate, in air. If the product has been fused, it is **litharge**; if not, **massicot**. It forms copper-colored, mica-like plates, or a yellow powder; or crystallizes, from its solution in soda or potash, in white, rhombic dodecahedra, or in rose-colored cubes. It fuses near a red heat, and volatilizes at a white heat; sp. gr. 9.277—9.5. It is sparingly soluble in H_2O , forming an alkaline solution.

Heated in air to 300° it is oxidized to **minium**. It is readily reduced by H or C. With Cl it forms $PbCl_2$ and O. It is a strong base; decomposes alkaline salts, with liberation of the alkali. It dissolves in HNO_3 , and in hot acetic acid, as nitrate or acetate. When ground up with oils it saponifies the glycerol ethers, the Pb combining with the fatty acids to form Pb soaps, one of which, **lead oleate**, is the **emplastrum plumbi**, *lead plaster*, *diachylon plaster* (U. S. P.). It also combines with the alkalies and earths to form **plumbites**. **Calcium plumbite**, $CaPb_2O_3$, is a crystalline salt, formed by heating PbO with milk of lime, and used in solution as a hair dye.

Plumboso-plumbic Oxide—*Red oxide*—**Minium**—**Red lead**— Pb_3O_4 —685—is prepared by heating massicot to 300° in air. It ordinarily has the composition Pb_3O_4 , and has been considered as composed of PbO_2 , $2PbO$; or a basic lead salt of plumbic acid, PbO_3Pb , PbO . An orange-colored variety is formed when lead carbonate is heated to 300° .

It is a bright red powder, sp. gr. 8.62. It is converted into PbO when strongly heated, or by the action of reducing agents. HNO_3 changes its color to brown, dissolving PbO and leaving PbO_2 . It is decomposed by HCl, with formation of $PbCl_2$, H_2O and Cl.

Lead Dioxide.—*Plumbic anhydride*— PbO_2 —239—is prepared, either by dissolving the PbO out of red lead by dilute HNO_3 , or by passing a current of Cl through H_2O , holding lead carbonate in suspension.

It is a dark, reddish brown, amorphous powder; sp. gr. 8.903–9.190; insoluble in H_2O . Heated, it loses half its O, and is converted

into PbO . It is a valuable oxidant. It absorbs SO_2 to form PbSO_4 . It combines with alkalis to form **plumbates**, M_2PbO_3 .

Lead Sulphide—Galena— PbS —239—exists in nature. It is also formed by direct union of Pb and S ; by heating PbO with S , or vapor of CS_2 ; or by decomposing a solution of a Pb salt by H_2S or an alkaline sulphide.

The native sulphide is a bluish gray, and has a metallic luster; sp. gr. 7.58; that formed by precipitation is a black powder; sp. gr. 6.924. It fuses at a red heat and is partly sublimed, partly converted into a subsulphate. Heated in air it is converted into PbSO_4 , PbO and SO_2 . Heated in H it is reduced. Hot HNO_3 oxidizes it to PbSO_4 . Hot HCl converts it into PbCl_2 . Boiling H_2SO_4 converts it into PbSO_4 and SO_2 .

Lead Chloride— PbCl_2 —278—is formed by the action of Cl upon Pb at a red heat; by the action of boiling HCl upon Pb , and by double decomposition between a lead salt and a chloride.

It crystallizes in plates, or hexagonal needles; sparingly soluble in cold H_2O , less soluble in H_2O containing HCl ; more soluble in hot H_2O , and in concentrated HCl .

Several oxychlorides are known. **Cassel, Paris, Verona, or Turner's yellow** is $\text{PbCl}_2, 7\text{PbO}$.

Lead Iodide— PbI_2 —461—is deposited, as a bright yellow powder, when a solution of potassium iodide is added to a solution of Pb salt. Fused in air, it is converted into an oxyiodide. Light and moisture decompose it, with liberation of I . It is almost insoluble in H_2O , soluble in solutions of ammonium chloride, sodium hyposulphite, alkaline iodide, and potash.

Salts of Lead.—Nitrates.—Lead Nitrate— $\text{Pb}(\text{NO}_3)_2$ —is formed by solution of Pb , or of its oxides, in excess of HNO_3 . It forms anhydrous crystals; soluble in H_2O . Heated, it is decomposed into PbO , O and NO_2 .

Lead Sulphate— PbSO_4 —303—is formed by the action of hot concentrated H_2SO_4 on Pb ; or by double decomposition between a sulphate and a Pb salt in solution. It is a white powder, almost insoluble in H_2O , soluble in concentrated H_2SO_4 , from which it is deposited by dilution.

Lead Chromate—Chrome yellow— PbCrO_4 —323—is formed by decomposing $\text{Pb}(\text{NO}_3)_2$ with potassium chromate. It is a yellow, amorphous powder, insoluble in H_2O , soluble in alkalis.

Acetates.—Lead Acetate—Salt of Saturn—Sugar of Lead—Plumbi acetate (U. S. P.)— $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{Aq}$ —325+54—is formed by dissolving PbO in acetic acid; or by exposing Pb in contact with acetic acid to air.

It crystallizes in large, oblique rhombic prisms, sweetish, with a metallic after-taste; soluble in H_2O and alcohol; its solutions being acid. In air it effloresces, and is superficially converted into carbonate. It fuses at 75.5° ; loses Aq and a part of its acid at 100° , forming the sesquibasic acetate, $2[\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2]\text{Pb}(\text{OH})_2$; at 280°

it enters into true fusion, and, at a slightly higher temperature, is decomposed into CO_2 , Pb, and acetone. Its aqueous solution dissolves PbO , with formation of basic acetates.

Sexbasic Lead Acetate— $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)\text{OH}$, 2PbO —729—is the main constituent of **Goulard's extract**=**Liquor plumbi subacetatis** (U. S. P.), and is formed by boiling a solution of the neutral acetate with PbO in fine powder. It contains 18 per cent. of Pb. The solution becomes milky on addition of ordinary H_2O , from formation of the sulphate and carbonate. The **liquor plumbi subacetatis dilutus** (U. S. P.) contains 4 parts of the liquor plumbi subacetatis in 100 parts of water.

Lead Carbonate— PbCO_3 —267—occurs in nature as **cerusite**; and is formed, as a white, insoluble powder, when a solution of a Pb compound is decomposed by an alkaline carbonate, or by passing CO_2 through a solution containing Pb.

White lead or **ceruse**, or **plumbi carbonas**, is a basic carbonate $(\text{PbCO}_3)_2$, $\text{Pb}(\text{OH})_2$ —775—mixed with varying proportions of other basic carbonates. It is usually prepared by the action of CO_2 on a solution of the subacetate, prepared by the action of acetic acid on Pb and PbO . It is a heavy, white powder, insoluble in H_2O , except in the presence of CO_2 ; soluble in acids with effervescence; and decomposed by heat into CO_2 and PbO . White lead enters into the composition of almost all oil-paints, being used to dilute other pigments. The darkening of oil-paintings is due to the formation of the black lead sulphide by atmospheric H_2S .

Analytical Characters.—(1) Hydrogen sulphide, in acid solution: a black ppt.; insoluble in alkaline sulphides, and in cold, dilute acids. (2) Ammonium sulphhydrate: black ppt.; insoluble in excess. (3) Hydrochloric acid: white ppt., in not too dilute solution; soluble in boiling H_2O . (4) Ammonium hydroxide: white ppt.; insoluble in excess. (5) Potash: white ppt.; soluble in excess, especially when heated. (6) Sulphuric acid: white ppt.; insoluble in weak acids, soluble in solution of ammonium tartrate. (7) Potassium iodide: yellow ppt.; sparingly soluble in boiling H_2O ; soluble in large excess. (8) Potassium chromate: yellow ppt.; soluble in KOH solution. (9) Iron or zinc separate the element from solution of its salts.

Action on the Economy.—All the soluble compounds of Pb, and those which, although not soluble, are readily convertible into soluble compounds by H_2O , air, or the digestive fluids, are actively poisonous. Some are also injurious by their local action upon tissues with which they come in contact; such are the acetate, and, in less degree, the nitrate.

The **chronic** form of lead intoxication, **painter's colic**, etc., is purely poisonous, and is produced by the continued absorption of minute quantities of Pb, either by the skin, lungs, or stomach. The **acute** form presents symptoms referable to the local, as well as to the poisonous, action of the Pb salt, and is usually caused by the ingestion of a single dose of the acetate or carbonate.

Metallie Pb, although probably not poisonous of itself, causes chronic lead-

poisoning by the readiness with which it is convertible into compounds capable of absorption. The principal sources of poisoning by metallic Pb are: the contamination of drinking water which has been in contact with the metal (see p. 67); the use of articles of food, or of chewing tobacco, which has been packed in tin-foil, containing an excess of Pb; the drinking of beer or other beverages which have been in contact with pewter; or the handling of the metal and its alloys.

Almost all the compounds of Pb may produce painter's colic. The carbonate, in painters, artists, manufacturers of white lead, and in persons sleeping in newly-painted rooms; the oxides, in the manufactures of glass, pottery, sealing-wax, and litharge, and by the use of lead-glazed pottery; by other compounds, by the inhalation of the dust of cloth factories, and by the use of lead hair-dyes.

Acute lead-poisoning is of by no means as common occurrence as the chronic form, and usually terminates in recovery. It is caused by the ingestion of a single dose of the acetate, subacetate, carbonate, or of red lead. In such cases the administration of magnesium sulphate is indicated; it enters into double decomposition with Pb salt to form the insoluble PbSO_4 .

Lead, once absorbed, is eliminated very slowly, it becoming fixed by combination with the proteins, a form of combination which is rendered soluble by potassium iodide. The channels of elimination are by the perspiration, urine and bile.

V. BISMUTH GROUP.

BISMUTH.

Symbol=Bi—*Atomic weight*=208—*Molecular weight*=416.—*Sp. gr.*=9.677–9.935.

This element is usually classed with Sb; by some writers among the metals, by others in the phosphorus group. We are led to class Bi in our fourth class, and in a group alone, because: (1) while the so-called salts of Sb are not salts of the element, but of the radical $(\text{SbO})'$, *antimonyl*, Bi enters into saline combination, not only in the radical **bismuthyl** $(\text{BiO})'$, but also as an element; (2) while the compounds of the elements of the N group in which those elements are quinquivalent are, as a rule, more stable than those in which they are trivalent, Bi is trivalent in all its known compounds except one, which is very unstable, in which it is quinquivalent; (3) the hydrates of the N group are strongly acid, and their corresponding salts are stable and well defined; but those hydrates of Bi which are acid are but feebly so, and the bismuthates are unstable; (4) no compound of Bi and H is known.

Occurrence.—Occurs principally free, also as Bi_2O_3 and Bi_2S_3 .

Properties.—Crystallizes in brilliant, metallic rhombohedra; hard and brittle.

It is only superficially oxidized in cold air. Heated to redness in air, it becomes coated with a yellow film of oxide. In H_2O , containing CO_2 , it forms a crystalline subcarbonate. It combines directly with

Cl, Br and I. It dissolves in hot H_2SO_4 as sulphate, and in HNO_3 as nitrate.

It is usually contaminated with As, from which it is best purified by heating to redness a mixture of powdered bismuth, potassium carbonate, soap and charcoal, under a layer of charcoal. After an hour the mass is cooled; the button is separated and fused until its surface begins to be coated with a yellowish brown oxide.

Oxides.—Four oxides are known: Bi_2O_2 , Bi_2O_3 , Bi_2O_4 , and Bi_2O_5 .

Bismuth Trioxide—*Bismuthous oxide*— Bi_2O_3 —464—is formed by heating Bi, or its nitrate, carbonate or hydrate. It is a pale yellow, insoluble powder; sp. gr. 8.2; fuses at a red heat; soluble in HCl , HNO_3 and H_2SO_4 and in fused potash. **Magma bismuthi** (U. S. P.)—bismuth magma—milk of bismuth—contains about 6 per cent. of Bi_2O_3 .

Hydrates.—Bismuth forms at least four hydrates.

Bismuthous Hydroxide— $\text{Bi}(\text{OH})_3$ —259—is formed, as a white precipitate, when potash or ammonium hydroxide is added to a cold solution of a Bi salt. When dried it loses H_2O , and is converted into **Bismuthyl hydroxide** $(\text{BiO})\text{OH}$.

Bismuth Trichloride—*Bismuthous chloride*— BiCl_3 —314.5—is formed by heating Bi in Cl ; by distilling a mixture of Bi and mercuric chloride; or by distilling a solution of Bi in aqua regia. It is a fusible, volatile, deliquescent solid; soluble in dilute HCl . On contact with H_2O it is decomposed with formation of **bismuthyl chloride**, $(\text{BiO})\text{Cl}$, or **pearl white**.

Bismuth Nitrate— $\text{Bi}(\text{NO}_3)_3 + 5 \text{ Aq}$ —394+90—obtained by dissolving Bi in HNO_3 . It crystallizes in large, colorless prisms; at 150° , or by contact with H_2O , it is converted into bismuthyl nitrate; at 260° into Bi_2O_3 .

Bismuthyl Nitrate—*Trinitrate* or *subnitrate of bismuth*—*Flake white*—**Bismuthi subnitras**—(U. S. P.)— $(\text{BiO})\text{NO}_3 \cdot \text{H}_2\text{O}$ —304—is formed by decomposing a solution of $\text{Bi}(\text{NO}_3)_3$ with a large quantity of H_2O . It is a white, heavy, faintly acid powder; soluble to a slight extent in H_2O when freshly precipitated, the solution depositing it again on standing. It is decomposed by pure H_2O , but not by H_2O containing $\frac{1}{500}$ ammonium nitrate. It usually contains 1 Aq, which it loses at 100° . Bismuth subnitrate, as well as the subcarbonate, is liable to contamination with arsenic, which accompanies bismuth in its ores.

Bismuthyl Carbonate—**Bismuth subcarbonate**—**Bismuthi subcarbonas** (U. S. P.)— $(\text{BiO})_2\text{CO}_3 \cdot \text{H}_2\text{O}$ —526—is a white or yellowish, amorphous powder, formed when a solution of an alkaline carbonate is added to a solution of $\text{Bi}(\text{NO}_3)_3$. It is odorless, tasteless, and insoluble in H_2O and in alcohol.

When heated to 100° , it loses H_2O , and is converted into

$(\text{BiO})_2\text{CO}_3$. At a higher temperature it is further decomposed into Bi_2O_3 and CO_2 .

The relation of the salts of bismuth to the bismuthyl salts, may be seen in the following table:

	BISMUTH	BISMUTHYL
Chloride	BiCl_3	$(\text{BiO})\text{Cl}$
Bromide	BiBr_3	$(\text{BiO})\text{Br}$
Nitrate	$\text{Bi}(\text{NO}_3)_3$	$(\text{BiO})\text{NO}_3$
Sulphate	$(\text{Bi})_2(\text{SO}_4)_3$	$(\text{BiO})_2\text{SO}_4$
Carbonate	$(\text{Bi})_2(\text{CO}_3)_3$	$(\text{BiO})_2\text{CO}_3$

Analytical Characters.—(1) Water: white ppt., even in presence of tartaric acid, but not of HNO_3 , HCl , or H_2SO_4 . (2) Hydrogen sulphide, black ppt., insoluble in dilute acids and in alkaline sulphides. (3) Ammonium sulphhydrate: black ppt., insoluble in excess. (4) Potash, soda, or ammonia: white ppt., insoluble in excess, and in tartaric acid; turns yellow when the liquid is boiled. (5) Potassium ferrocyanide: yellowish ppt., insoluble in HCl . (6) Potassium ferricyanide: yellowish ppt., soluble in HCl . (7) Infusion of galls: orange ppt. (8) Potassium iodide: brown ppt., soluble in excess. (9) Reacts with Reinsch's test (*q. v.*), but gives no sublimate in the glass tube.

Action on the Economy.—Although the medicinal compounds of bismuth are probably poisonous, if taken in sufficient quantity, the ill effects ascribed to them are in most, if not all cases, referable to contamination with arsenic. Symptoms of arsenical poisoning have been frequently observed when the subnitrate has been taken internally, and also when it has been used as a cosmetic. Bismuth subnitrate is frequently administered by physicians in cases of arsenical poisoning, not recognized as such during life.

When preparations of bismuth are administered, the alvine discharges contain bismuth sulphide, as a dark brown powder.

VI. TIN GROUP.

TITANIUM—ZIRCONIUM—TIN

Ti and Sn are bivalent in one series of compounds, SnCl_2 , and quadrivalent in another, SnCl_4 . Zr, so far as known, is always quadrivalent. Each of these elements forms an acid (or salts corresponding to one) of the composition of H_2MO_3 , and a series of oxy-salts of the composition of $\text{M}^{\text{iv}}(\text{NO}_3)_4$.

TITANIUM.

Symbol = Ti—*Atomic weight* = 48—(*International* = 48.1) — *Sp. gr.* = 5.3.

Occurs in clays and iron ores, and as TiO_2 in several minerals. **Titanic anhydride**, TiO_2 , is a white, insoluble, infusible powder, used in the manufacture of artificial teeth; dissolves in fused KOH, as potassium titanate. Titanium combines readily with N, which it absorbs from air when heated. When NH_3 is passed over red-hot TiO_2 , it is decomposed with formation of the violet nitride, TiN_2 . Another compound of Ti and N forms hard, copper-colored, cubical crystals.

ZIRCONIUM.

Symbol = Zr—*Atomic weight* = 90—(*International* = 90.6)—*Sp. gr.* = 4.15.

Occurs in zircon and hyacinth. Its oxide, **zirconia**, ZrO_2 , is a white powder, insoluble in KOH. Being infusible, and not altered by exposure to air, it is used in pencils to replace lime in the calcium light.

TIN.

Symbol = Sn (*Stannum*)—*Atomic weight* = 118.5—(*International* = 118.7)—*Molecular weight* = 237.—*Sp. gr.* = 7.285–7.293.

Tin is bivalent in one series of compounds, SnCl_2 ; and quadrivalent in another, SnCl_4 .

Occurrence.—As **tinstone** (SnO_2) or **cassiterite**, and in **stream tin**.

Preparation.—The commercial metal is prepared by roasting the ore, extracting with H_2O , reducing the residue by heating with charcoal, and refining.

Pure tin is obtained by dissolving the metal in HCl; filtering; evaporating; dissolving the residue in H_2O ; decomposing with ammonium carbonate; and reducing the oxide with charcoal.

Properties.—A soft, malleable, bluish white metal; but slightly tenacious; emits a peculiar sound, the **tin-cry**, when bent. A good conductor of heat and electricity. Air affects it but little, except when it is heated; more rapidly if Sn is alloyed with Pb. It oxidizes slowly in H_2O ; more rapidly in the presence of sodium chloride. Its presence with Pb accelerates the action of H_2O upon the latter. It dissolves in HCl as SnCl_2 . In presence of a small quantity of H_2O , HNO_3 converts it into metastannic acid. Alkaline solutions dissolve it as metastannates. It combines directly with Cl, Br, I, S, P and As.

Tin plates are thin sheets of Fe, coated with Sn. **Tin foil** consists of thin laminae of Sn, frequently alloyed with Pb. Copper and iron vessels are **tinned** after brightening, by contact with molten Sn. Pewter, bronze, bell metal, gun metal, britannia metal, speculum metal, type metal, solder, and fusible metal, contain Sn.

Oxides.—**Stannous Oxide**— SnO —134.5—obtained by heating the hydroxide or oxalate without contact of air. It is a white, amorphous powder, soluble in acids, and in hot, concentrated solution of potash. It absorbs O readily.

Stannic Oxide— SnO_2 —150.5—occurs native as *tinestone* or *cassiterite*, and is formed when Sn or SnO is heated in air. It is used as a polishing material, under the name of **putty powder**.

Hydrates.—**Stannous Hydroxide**— $\text{Sn}(\text{OH})_2$ —152.5—is a white precipitate, formed by alkaline hydroxides and carbonates in solution of SnCl_2 .

Stannic Acid— H_2SnO_3 —168.5—is formed by the action of alkaline hydroxides on solutions of SnCl_4 . It dissolves in solutions of the alkaline hydroxides, forming **stannates**.

Metastannic Acid— $\text{H}_2\text{Sn}_5\text{O}_{11}$ —770.5—is a white, insoluble powder, formed by acting on Sn with HNO_3 .

Chlorides.—**Stannous Chloride**—**Tin crystals**.— $\text{SnCl}_2 + 2 \text{Aq}$ —189.5+36—is obtained by dissolving Sn in HCl. It crystallizes in colorless prisms; soluble in a small quantity of H_2O ; decomposed by a large quantity, unless in the presence of free HCl, with formation of an oxychloride. Loses its Aq at 100° . In air it is transformed into stannic chloride and oxychloride. Oxidizing and chlorinating agents convert it into SnCl_4 . It is a strong reducing agent.

Stannic Chloride—*Bichloride*— SnCl_4 —260.5—is formed by acting on Sn or SnCl_2 with Cl, or by heating Sn in aqua regia. It is a fuming, yellowish liquid; sp. gr. 2.28; boils at 120° .

Analytical Characters.—**STANNOUS.**—(1) Potash, or soda: white ppt.; soluble in excess; the solution deposits Sn when boiled. (2) Ammonium hydroxide: white ppt; insoluble in excess; turns olive-brown when the liquid is boiled. (3) Hydrogen sulphide: dark brown ppt.; soluble in KOH, alkaline sulphides, and hot H_2O . (4) Mercuric chloride: white ppt., turning gray and black. (5) Auric chloride: purple or brown ppt., in presence of small quantities of HNO_3 . (6) Zinc: deposit of Sn.

STANNIC.—(1) Potash, or ammonia: white ppt.; soluble in excess. (2) Hydrogen sulphide: yellow ppt.; soluble in alkalies, alkaline sulphides, and hot HCl. (3) Sodium hyposulphite: yellow ppt., when heated.

VII. PLATINUM GROUP.

PALLADIUM. PLATINUM.

VIII. RHODIUM GROUP.

RHODIUM. RUTHENIUM. IRIDIUM.

The elements of these two groups, together with osmium, are usually classed as “metals of the platinum ores.” They all form hydrates (or salts representing them) having acid properties. Osmium has been removed, because the relations existing between its compounds, and those of molybdenum and tungsten, are much closer than those which they exhibit to the compounds of these groups. The separation of the remaining platinum metals into two groups is based upon resemblances in the composition of their compounds, as shown in the following tables:

CHLORIDES.

PdCl ₂PtCl ₂	RhCl ₂RuCl ₂ ?
PdCl ₄PtCl ₄	——.....RuCl ₄IrCl ₄
——.....——	Rh ₂ Cl ₆Ru ₂ Cl ₆Ir ₂ Cl ₆

OXIDES.

PdOPtO	RhORuOIrO
——.....——	Rh ₂ O ₃ Ru ₂ O ₃Ir ₂ O ₃
PdO ₂PtO ₂	RhO ₂RuO ₂IrO ₂
——.....——	RhO ₃RuO ₃IrO ₃
——.....——	——RuO ₄——

PLATINUM.

Symbol=Pt—*Atomic weight*=195—(*International*=195.2)—*Molecular weight*=390—*Sp. gr.*=21.1–21.5.

Occurrence.—Free and alloyed with Os, Ir, Pd, Rh, Ru, Fe, Pb, Au, Ag and Cu.

Properties.—The compact metal has a silvery luster; softens at a white heat; may be welded; fuses with difficulty; highly malleable, ductile and tenacious. **Spongy platinum** is a grayish, porous mass, formed by heating the double chloride of Pt and NH₄. **Platinum black** is a black powder, formed by dissolving PtCl₂ in solution of potash, and heating with alcohol. Both platinum black and platinum sponge are capable of condensing large quantities of gas, and act as indirect oxidants.

Platinum is not oxidized by air or O; it combines directly with Cl, P, As, Si, S, and C; is not attacked by acids, except aqua regia, in which it dissolves. It forms fusible alloys when heated with metals or reducible metallic oxides. It is attacked by mixtures liberating Cl, and by contact with heated phosphates, silicates, hydroxides, nitrates, or carbonates of the alkaline metals.

Platinic Chloride—*Tetrachloride of platinum*— PtCl_4 —337—When Pt is dissolved in aqua regia and the solution is evaporated, red, deliquescent crystals of **hydrochloroplatinic acid**, H_2PtCl_6 , are obtained. These, when heated in chlorine, yield yellow, non-deliquescent crystals of platinic chloride, PtCl_4 . Hydrochloroplatinic acid is a strong dibasic acid, the platinum being in the anion, which forms crystalline **chloroplatinates** with the alkaline metals, NH_4 , and a great number of nitrogenous organic bases. The formation of the K and NH_4 salts is utilized to test for those cations, and the formation of the organic compounds is resorted to for the identification and analysis of these bases.

CLASS V.—BASYLOUS ELEMENTS.

Elements whose Oxides unite with Water to form Bases; never to form Acids. Which form Oxysalts.

The elements of this class are essentially basic and electropositive. In solutions of their compounds they never occur in an anion, simple or compound, but always constitute simple cations.

I. SODIUM GROUP.

Alkali Metals.

LITHIUM—SODIUM—POTASSIUM—RUBIDIUM—CÆSIUM—SILVER.

Each of the elements of this group forms a single chloride, $M'Cl$, and one or more oxides, the most stable of which has the composition M'_2O . They are, therefore, univalent. Their hydroxides, $M'OH$, are more or less alkaline and have markedly basic characters. Silver resembles the other members of the group in *chemical* properties, although it does not in *physical* characters.

The name “alkali,” first applied to “potash” from wood ashes (p. 160) is now used to designate substances which are strongly basic, are alkaline in reaction, and saponify fats. The **caustic alkalies** are the hydroxides of K and Na, the **carbonated alkalies** are their carbonates. **Volatile alkali** is ammonium hydroxide or carbonate.

LITHIUM.

Symbol=Li—*Atomic weight*=7—(*International*=6.94)—*Molecular weight*=14—*Sp. gr.*=0.589.

Occurrence.—Widely distributed in small quantity; in many minerals and mineral waters; in the ash of tobacco and other plants; in the milk and blood.

Properties.—A silver-white, ductile, volatile metal; the lightest of the solid elements; burns in air with a crimson flame; decomposes H_2O at ordinary temperatures, without igniting.

Lithium Chloride.— $LiCl$ —42.5—crystallizes in deliquescent, regular octahedra; very soluble in H_2O and in alcohol.

Lithium Bromide—*Lithii bromidum*—(U. S. P.)— $LiBr$ —87—is formed by decomposing lithium sulphate with potassium bromide; or by saturating a solution of HBr with lithium carbonate. It crystallizes in very deliquescent, soluble needles.

Lithium Carbonate—*Lithii carbonas* (U. S. P.)— Li_2CO_3 —74—is a white, sparingly soluble, alkaline, amorphous powder. With uric acid it forms lithium urate, which is the most soluble of the urates of this class, and is therefore given to patients suffering from “the uric acid diathesis.”

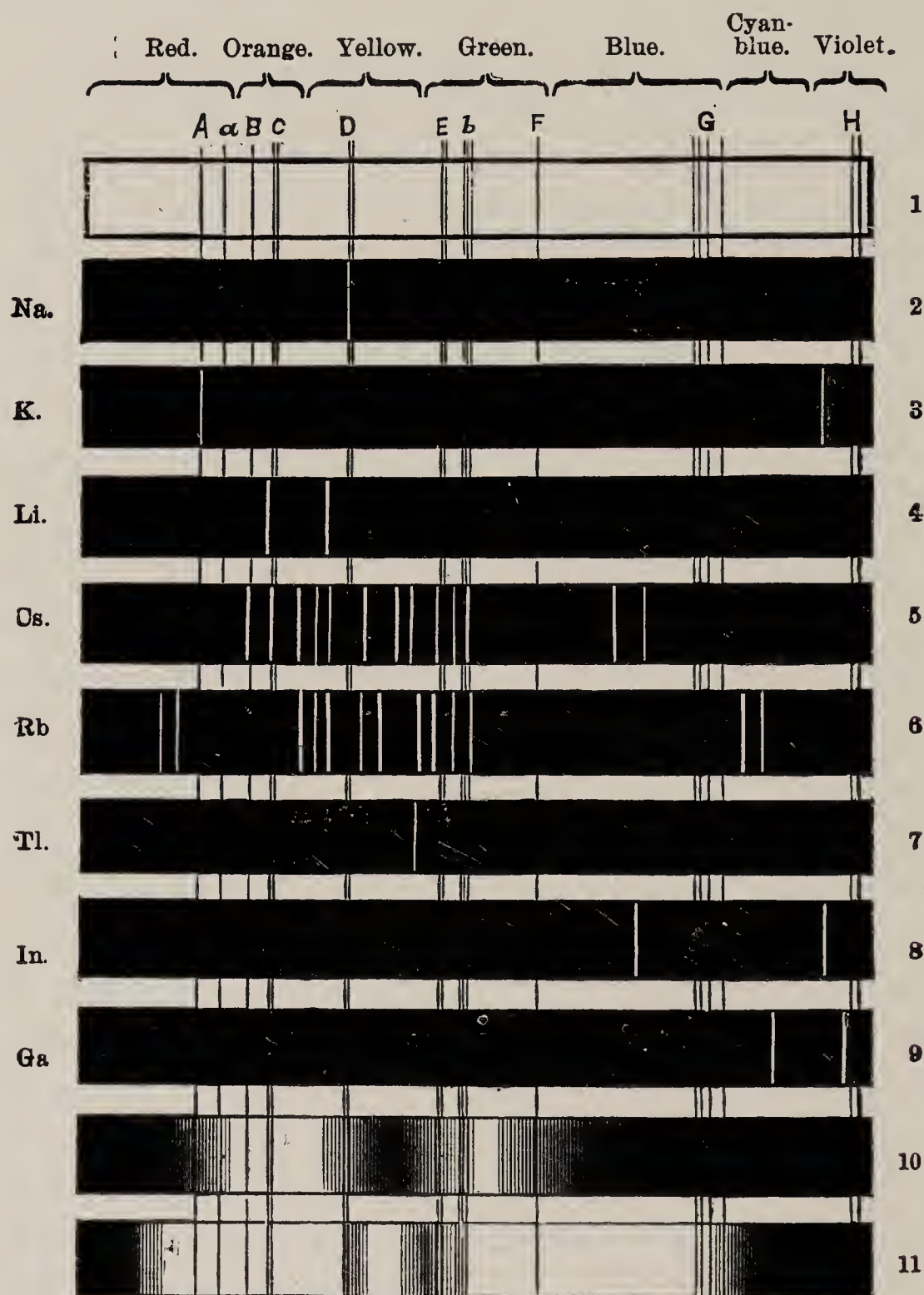


FIG. 16.—1, Solar spectrum; 10 and 11, Absorption spectra.

Lithium bicarbonate— LiHCO_3 —68—is the salt which is present in *lithia water*. It is derived from the carbonate:



Analytical Characters.—(1) Ammonium carbonate: white ppt. in concentrated solutions; not in dilute solutions, or in presence of ammoniacal salts. (2) Sodium phosphate: white ppt. in neutral or alkaline solution; soluble in acids and in solutions of ammoniacal

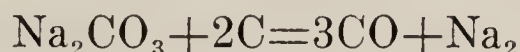
salts. (3) It colors the Bunsen flame red; and exhibits a spectrum of two lines— $\lambda = 6705$ and 6102 (Fig. 16, No. 4, p. 150).

SODIUM.

Symbol=Na (*Natrium*)—*Atomic weight*=23—(*International*=23.00)—*Molecular weight*=46—*Sp. gr.*=0.972.

Occurrence.—As chloride, very abundantly and widely distributed; also as carbonate, nitrate, sulphate, borate, etc.

Preparation.—By heating a mixture of dry sodium carbonate, chalk, and charcoal to whiteness in iron retorts:



It is now manufactured by the electrolysis of fused NaOH.

Properties.—A silver-white metal, rapidly tarnished, and coated with a yellow film in air. Waxy at ordinary temperatures; volatile at a white heat, forming a colorless vapor, which burns in air with a yellow flame.

It oxidizes in air, and is usually preserved under naphtha. It burns with a yellow flame. It combines directly with Cl, Br, I, S, P, As, Pb and Sn. It decomposes water with evolution of hydrogen: $\text{Na}_2 + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$. Because of this and other similar reactions, metallic sodium, either as such or in the diluted form of sodium amalgam, is largely used to effect reductions.

Oxides.—Two oxides are known: **Sodium monoxide**— Na_2O —a grayish white mass; formed when Na is burnt in dry air, or by the action of Na on NaOH. **Sodium dioxide**— Na_2O_2 —a white solid, formed when Na is heated in dry air to 200° . Sodium dioxide, or peroxide, is now manufactured by oxidizing the fused metal in dry air or oxygen, and is used as a bleaching and oxidizing agent. It is a yellowish white, amorphous, very hygroscopic powder. If the temperature is kept low it dissolves in dilute acids, forming a strong solution of hydrogen dioxide: $\text{Na}_2\text{O}_2 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O}_2$. With water it produces a great elevation of temperature and liberates nascent oxygen: $2\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} = 4\text{NaOH} + \text{O}_2$. With magnesium sulphate it forms magnesium dioxide, a non-alkaline oxidant: $\text{Na}_2\text{O}_2 + \text{MgSO}_4 = \text{Na}_2\text{SO}_4 + \text{MgO}_2$.

Sodium Hydroxide—*Sodium hydrate*—**Caustic Soda**—**Sodium Hydroxidum** (U. S. P.)— NaOH —40—is formed: (1) When H_2O is decomposed by Na; (2) by decomposing sodium carbonate by calcium hydroxide: $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 = \text{CO}_3\text{Ca} + 2\text{NaOH}$ (soda by lime); (3) in the same manner as in (2), using barium hydroxide in place of lime (soda by baryta). It frequently contains considerable quantities of As.

It is an opaque, white, fibrous, brittle solid; fusible below redness; sp, gr. 2.00; very soluble in H_2O , forming strongly alkaline

and caustic solutions, **soda lye** and **liquor sodii hydroxidi**, U. S. P., (containing not less than 4.5 per cent. of NaOH). When exposed to air, solid or in solution, it absorbs H_2O and CO_2 , and is converted into carbonate. Its solutions attack glass.

Sodium Chloride—Common salt—Sea salt—Table salt—Sodii chloridum (U. S. P.)— NaCl —58.5—occurs very abundantly in nature, deposited in the solid form as **rock salt**; in solution in all natural waters, especially in sea and mineral spring waters; in suspension in the atmosphere; and as a constituent of almost all animal and vegetable tissues and fluids. It is formed in an infinite variety of chemical reactions. It is obtained from rock salt, or from the waters of the sea, or of saline springs; and is the source from which all the Na compounds are usually obtained, directly or indirectly.

It crystallizes in anhydrous, white cubes, or octahedra; sp. gr. 2.078; fuses at a red heat, and crystallizes on cooling; sensibly volatile at a white heat; quite soluble in H_2O , the solubility varying but slightly with the variations of temperature. Dilute solutions yield almost pure ice on freezing. It is precipitated from concentrated solutions by HCl . It is insoluble in absolute alcohol; sparingly soluble in dilute spirit. It is decomposed by H_2SO_4 with formation of HCl and sodium sulphate: $2\text{NaCl} + \text{H}_2\text{SO}_4 = 2\text{HCl} + \text{Na}_2\text{SO}_4$.

Physiological salt solution (*Liquor sodii chloridi physiologicus*, U. S. P.) contains 8.5 gms. of NaCl in a liter of distilled water.

Sodium Bromide—Sodii bromidum (U. S. P.)— NaBr —103—is formed by dissolving Br in solution of NaOH to saturation; evaporating; calcining at dull redness; redissolving, filtering, and crystallizing. It crystallizes in anhydrous cubes; quite soluble in H_2O , soluble in alcohol.

Sodium Iodide—Sodii iodidum (U. S. P.)— NaI —150—is prepared by heating together H_2O , Fe, and I in fine powder; filtering; adding an equivalent quantity of sodium sulphate, and some slaked lime, boiling, decanting and evaporating. Crystallizes in anhydrous cubes; very soluble in H_2O ; soluble in alcohol.

Sodium Nitrate—Cubic or Chili saltpeter— NaNO_3 —85—occurs in natural deposits in Chili and Peru. It crystallizes in anhydrous, deliquescent rhombohedra; cooling and somewhat bitter in taste; fuses at 310° ; very soluble in H_2O . Heated with H_2SO_4 , it is decomposed, yielding HNO_3 and hydrosodic sulphate: $\text{H}_2\text{SO}_4 + \text{NaNO}_3 = \text{HNaSO}_4 + \text{HNO}_3$. This reaction is that used for obtaining HNO_3 .

Sulphates.—Monosodic Sulphate—Hydrosodic sulphate—Acid sodium sulphate—Bisulphate— HNaSO_4 —120—crystallizes in long, four-sided prisms; is unstable and decomposed by air, H_2O or alcohol, into H_2SO_4 and Na_2SO_4 . Heated to dull redness it is converted into **sodium pyrosulphate**, $\text{Na}_2\text{S}_2\text{O}_7$, corresponding to Nordhausen sulphuric acid.

Disodic Sulphate—Sodium sulphate—Neutral sodium sulphate—

Glauber's salt—Sodii sulphas (U. S. P.)— $\text{Na}_2\text{SO}_4 + \text{Aq} - 142 + 18$ —occurs in nature in solid deposits, and in solution in natural waters. It is obtained as a secondary product in the manufacture of HCl, by the action of H_2SO_4 on NaCl, the decomposition occurring according to the equation: $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$, if the temperature is raised sufficiently. At lower temperatures, the monosodic salt is produced, with only half the yield of HCl: $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HCl}$.

It crystallizes with 7 Aq, from saturated or supersaturated solutions at 5° ; or, more usually, with 10 Aq. As usually met with it is in large, colorless, oblique, rhombic prisms with 10 Aq; which effloresce in air, and gradually lose all their Aq. It fuses at 33° in its Aq, which it gradually loses. If fused at 33° and allowed to cool, it remains liquid in *supersaturated* solution, from which it is deposited, the entire mass becoming solid, on contact with a small particle of solid matter. It dissolves in HCl with considerable diminution of temperature.

Sodium Sulphite— $\text{Na}_2\text{SO}_3 + 7 \text{ Aq} - 126 + 126$ —is formed by passing SO_2 over crystallized Na_2CO_3 . It crystallizes in efflorescent, oblique prisms; quite soluble in H_2O , forming an alkaline solution. It acts as a reducing agent.

Sodium Thiosulphate—Sodium hyposulphite—Sodii thiosulphas (U. S. P.)— $\text{Na}_2\text{S}_2\text{O}_3 + 5 \text{ Aq} - 158 + 90$ —is obtained by dissolving S in hot concentrated solution of Na_2SO_3 , and crystallizing.

It forms large, colorless, efflorescent prisms; fuses at 45° ; very soluble in H_2O , insoluble in alcohol. Its solutions precipitate alumina from solutions of Al salts, without precipitating Fe or Mn; they dissolve many compounds insoluble in H_2O ; cuprous hydroxide, iodides of Pb, Ag and Hg, sulphides of Ca and Pb. It is used in photography as a fixing bath, and is called "hypo"; it acts as a disinfectant and antiseptic; it is also employed in bleaching, to remove the chlorine. H_2SO_4 decomposes $\text{Na}_2\text{S}_2\text{O}_3$ according to the equation:



and most other acids behave similarly. Oxalic, and a few other acids, decompose the thiosulphate with formation of H_2S as well as SO_2 and S.

Silicates.—Quite a number of silicates of Na are known. If silica and Na_2CO_3 are fused together, the residue extracted with H_2O , and the solution evaporated, a transparent, glass-like mass, soluble in warm water, remains; this is **soluble glass** or **water glass**. Exposed to air in contact with stone, it becomes insoluble, and forms an impermeable coating.

Phosphates.—**Trisodic Phosphate—Basic sodium phosphate**— $\text{Na}_3\text{PO}_4 + 12 \text{ Aq} - 164 + 216$ —is obtained by adding NaOH to disodic phosphate solution, and crystallizing. It forms six-sided prisms;

quite soluble in H_2O . Its solution is alkaline, and, on exposure to air, absorbs CO_2 , with formation of HNa_2PO_4 and Na_2CO_3 .

Disodic Phosphate—*Sodium phosphate*—*Hydro-disodic phosphate*—*Neutral sodium phosphate*—*Phosphate of soda*—**Sodii phosphas** (U. S. P.)— $\text{HNa}_2\text{PO}_4 + 12 \text{ Aq} - 142 + 216$ —is obtained by converting tricalcic phosphate into monocalcic phosphate, and decomposing that salt with sodium carbonate:



Below 30° it crystallizes in oblique rhombic prisms, with 12 Aq; at 33° it crystallizes with 7 Aq. The salt with 12 Aq effloresces in air, and parts with 5 Aq; and is very soluble in H_2O . The salt with 7 Aq is not efflorescent, and less soluble in H_2O . Its solutions are faintly alkaline.

Monosodic Phosphate—*Acid sodium phosphate*— $\text{H}_2\text{NaPO}_4 + \text{Aq} - 120 + 18$ —crystallizes in rhombic prisms; forming acid solutions. At 100° it loses Aq; at 200° it is converted into **acid pyrophosphate**, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$; and at 204° into the **metaphosphate**, NaPO_3 .

Sodium Arsenites.—The disodic arsenite, Na_2HAsO_3 , is obtained as a viscous mass by fusing together 1 molecule of As_2O_3 and 2 molecules of Na_2CO_3 without contact of air. The monosodic arsenite, NaH_2AsO_3 , is formed when an aqueous solution of Na_2CO_3 is boiled with As_2O_3 . By prolonged boiling this is converted into the pyroarsenite, $\text{Na}_2\text{H}_2\text{As}_2\text{O}_5$, and this into the metarsenite, NaAsO_2 , by progressive loss of water. Sodium arsenites exist in embalming liquids and are used in dyeing.

Sodium Arsenates.—The three arsenates, NaH_2AsO_4 , Na_2HAsO_4 , and Na_3AsO_4 corresponding to the phosphates, are known, and are used in dyeing processes.

Disodic Tetraborate—*Sodium pyroborate*—*Borate of sodium*—**Borax**—**Sodii boras** (U. S. P.)— $\text{Na}_2\text{B}_4\text{O}_7 + 10 \text{ Aq} - 202 + 180$ —is prepared by boiling boric acid with Na_2CO_3 and crystallizing:



It crystallizes in hexagonal prisms with 10 Aq; permanent in moist air, but efflorescent in dry air; or in regular octahedra with 5 Aq, permanent in dry air. Either form, when heated, fuses in its Aq, swells considerably; at a red heat becomes anhydrous; and, on cooling, leaves a transparent, glass-like mass. When fused it is capable of dissolving many metallic oxides, forming variously colored masses, hence its use as a flux and in blow-pipe analysis.

Sodium Hypochlorite— $\text{NaClO} - 74.5$ —only known in solution—**Liquor sodæ chlorinatæ** (U. S. P.) or **Labarraque's solution**—obtained by decomposing a solution of chloride of lime by Na_2CO_3 . It is a valuable source of Cl, and is used as a bleaching and disinfecting agent. The pharmacopœial preparation should contain not less than 2.5 per cent. of available chlorine.

Sodium Chlorate— $\text{NaClO}_3 - 106.5$ —is manufactured industrially by treating milk of lime with Cl. The solution of calcium chloride and chlorate so obtained

is treated with Na_2SO_4 , after removal of part of the CaCl_2 by concentration and cooling to 12° . The NaClO_3 and NaCl formed are separated by taking advantage of the greater solubility of the former. NaClO_3 is soluble in its own weight of H_2O at 20° .

Sodium Permanganate— NaMnO_4 —142—prepared in the same way as the K salt (*q.v.*), which it resembles in its properties. It enters into the composition of **Condy's fluid**, and of "**chlorozone**," which contains NaMnO_4 and NaClO .

Sodium Acetate—**Sodii acetat** (U. S. P.)— $\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{Aq}$ —82+54—crystallizes in large, colorless prisms; acid and bitter in taste; quite soluble in H_2O , soluble in alcohol; loses its Aq in dry air, and absorbs it again from moist air. It may be prepared by saturating acetic acid with sodium carbonate:



Heated with soda lime, it yields marsh gas. The anhydrous salt, heated with H_2SO_4 , yields glacial acetic acid.

Carbonates.—Three are known: Na_2CO_3 , HNaCO_3 , and $\text{H}_2\text{Na}_4(\text{CO}_3)_3$.

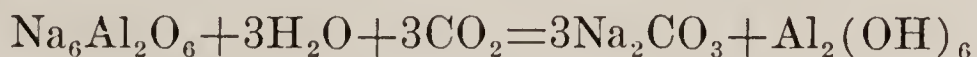
Disodic Carbonate—**Sodium carbonate**—*Neutral Carbonate*—*Soda*—**Sal soda**—**Washing Soda**—**Soda crystals**— $\text{Na}_2\text{CO}_3 + 10 \text{Aq}$ —106+180—industrially the most important of the Na compounds, is manufactured by Leblanc's or Solvay's processes; or from *cryolite*, a native fluoride of Na and Al.

Leblanc's process, in its present form, consists of three distinct processes: (1) The conversion of NaCl into the sulphate, by decomposition by H_2SO_4 . (2) The conversion of the sulphate into carbonate, by heating a mixture of the sulphate with calcium carbonate and charcoal. The product of this reaction, known as **black ball soda**, is a mixture of sodium carbonate with charcoal and calcium sulphide and oxide. (3) The purification of the product obtained in (2). The ball black is broken up, disintegrated by steam, and lixiviated. The solution on evaporation yields the **soda salt** or **soda** of commerce.

Of late years Leblanc's process has been in great part replaced by *Solvay's method*, or the *ammonia process*, which is more economical, and yields a purer product. In this process sodium chloride and ammonium bicarbonate react upon each other, with production of the sparingly soluble sodium bicarbonate, and the very soluble ammonium chloride. The sodium bicarbonate is then simply collected, dried, and heated, when it is decomposed into Na_2CO_3 , H_2O , and CO_2 . Sodium carbonate is also made from *cryolite*, a double fluoride of sodium and aluminium found in Greenland. This is heated with limestone when:



The sodium aluminate is extracted with water and the solution treated with carbon dioxide (obtained in the first reaction) when:



The monohydrated carbonate, *Sodii carbonas monohydratus* (U.

S. P.), $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ is a white, crystalline, granular powder. It combines with and dissolves in H_2O with elevation of temperature.

The crystalline sodium carbonate, $\text{Na}_2\text{CO}_3 + 10\text{Aq}$, forms large rhombic crystals, which effloresce rapidly in dry air; fuse in their Aq at 34° ; are soluble in H_2O , most abundantly at 38° . The solutions are alkaline in reaction.

Sodium Bicarbonate—Monosodic Carbonate—Bicarbonate of soda—Acid carbonate of soda—Vichy salt—Sodii bicarbonas (U. S. P.)— NaHCO_3 —84—exists in solution in many mineral waters. It is obtained by the action of CO_2 upon the disodic salt in the presence of H_2O ; or, as above described, by the Solvay method.

It crystallizes in rectangular prisms, anhydrous and permanent in dry air. In damp air it gives off CO_2 , and is converted into the **sesquicarbonate**, $\text{Na}_4\text{H}_2(\text{CO}_3)_3$. When heated it gives off CO_2 and H_2O , and leaves the disodic carbonate. Quite soluble in water; above 70° the solution gives off CO_2 . The solutions are alkaline.

Analytical Characters.—(1) Hydrofluosilicic acid: gelatinous ppt., if not too dilute. (2) Potassium pyroantimonate, in neutral solution, and in absence of metals other than K and Li: a white, flocculent ppt.; becoming crystalline on standing. (3) Periodic acid in excess: white ppt., in not too dilute solutions. (4) Colors the Bunsen flame yellow, and shows a brilliant double line at $\lambda = 5895$ and 5889 (Fig. 16, No. 2, p. 150).

POTASSIUM.

Symbol = K (*Kalium*)—*Atomic weight* = 39—(*International* = 39.10)—*Molecular weight* = 78—*Sp. gr.* = 0.865.

Potassium silicates are widely distributed in rocks and minerals. The ash of plants contains about 10 per cent. of potassium carbonate, and this was formerly the chief source of the K compounds. Almost all of these are now derived from the deposits of **carnallite**: KCl , $\text{MgCl}_2 + 6\text{Aq}$, and allied minerals at Stassfurt in Germany.

It is prepared by a process similar to that followed in obtaining Na; is a silver-white metal; brittle at 0° ; waxy at 15° ; fuses at 62.5° ; distils in green vapors at a red heat, condensing in cubic crystals. It is also obtained by electrolysis of fused KOH.

It is the only metal which oxidizes at low temperatures in dry air, in which it is rapidly coated with a white layer of oxide or hydroxide, and frequently ignites, burning with a violet flame. It must, therefore, be kept under naphtha. It decomposes H_2O , or ice, with great energy, the heat of the reaction igniting the liberated H. It combines with Cl with incandescence, and also unites directly with S, P, As, Sb, and Sn. Heated in CO_2 it is oxidized, and liberates C.

Oxides.—Three are known: K_2O ; K_2O_2 ; and K_2O_4 .

Potassium Hydroxide—Potassium hydrate—Potash—Potassa—

Caustic Potash—*Common caustic*—**Potassii hydroxidum** (U. S. P.)—KOH—56—is obtained by processes similar to those used in manufacturing NaOH. It is purified by solution in alcohol, evaporation and fusion in a silver basin, and casting in silver moulds—**potash by alcohol**; it is then free from KCl and K_2SO_4 , but contains small quantities of K_2CO_3 , and frequently As.

It is usually met with in cylindrical sticks, hard, white, opaque, and brittle. The KOH by alcohol has a bluish tinge, and a smoother surface than the common; sp. gr. 2.1; fuses at dull redness; is freely soluble in H_2O , forming a strongly alkaline and caustic liquid; less soluble in alcohol. In air, solid or in solution, it absorbs H_2O and CO_2 , and is converted into K_2CO_3 . Its solutions dissolve Cl, Br, I, S, and P. It decomposes the ammoniacal salts, with liberation of NH_3 ; and the salts of many of the metals, with formation of a K salt, and a metallic hydroxide. It dissolves the proteins, and, when heated, decomposes them with formation of leucin, tyrosin, etc. It oxidizes the carbohydrates with formation of potassium oxalate and carbonate. It decomposes the fats with formation of soft soaps.

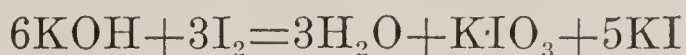
Solution of potassium hydroxide (*liquor potassii hydroxidi*, U. S. P.) or *liquor potassæ*, is an aqueous solution containing not less than 4.5 per cent of KOH.

Liver of Sulphur—*hepar sulphuris*—**potassa sulphurata** (U. S. P.)—is a mixture of K_2S_3 and $K_2S_2O_3$, and contains not less than 12.8 per cent. of sulphur.

Potassium Chloride—KCl—74.5—exists in nature, either pure or mixed with other chlorides; principally as **carnallite**, KCl, $MgCl_2 + 6 Aq$. It crystallizes in anhydrous, permanent cubes, soluble in H_2O .

Potassium Bromide—**Potassii bromidum** (U. S. P.)—KBr—119—is formed either by decomposing $FeBr_2$ by K_2CO_3 , or by dissolving Br in solution of KOH. In the latter case the **bromate** formed is converted into KBr, by calcination. It crystallizes in anhydrous cubes or tables; has a sharp, salty taste; very soluble in H_2O , sparingly so in alcohol. It is decomposed by Cl with liberation of Br.

Potassium Iodide—**Potassii iodidum** (U. S. P.)—KI—166—is obtained by saturating KOH solution with I, evaporating, and calcining the resulting mixture of iodide and iodate with charcoal:



It frequently contains iodate and carbonate. It crystallizes in cubes, transparent if pure; permanent in air; anhydrous; soluble in H_2O and in alcohol. It is decomposed by Cl, HNO_3 and HNO_2 with liberation of I. It combines with other iodides to form double iodides. Its solutions dissolve iodine and many metallic iodides.

Potassium Nitrate—**Nitre**—**Saltpeter**—**Potassii nitras** (U. S. P.)

— KNO_3 —101—occurs in nature, and is produced artificially, as a result of the decomposition of nitrogenized organic substances. It is usually obtained by decomposing native NaNO_3 by boiling solution of K_2CO_3 or KCl .

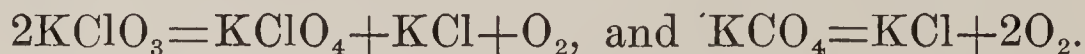
It crystallizes in six-sided, rhombic prisms, grooved upon the surface; soluble in H_2O , with depression of temperature; more soluble in H_2O containing NaCl ; very sparingly soluble in alcohol; fuses at 350° without decomposition; gives off O , and is converted into nitrite below redness; more strongly heated, it is decomposed into N , O , and a mixture of K oxides. It is a valuable oxidant at high temperatures. Heated with charcoal it deflagrates.

Gunpowder is an intimate mixture of KNO_3 with S and C , in such proportion that the KNO_3 yields all the O required for the combustion of the S and C .

Potassium Hypochlorite— KClO —90.5—is formed in solution by imperfect saturation of a cooled solution of KOH with hypochlorous acid. An impure solution is used in bleaching, and is known as **Javelle water**, which is the equivalent of the *liquor potassæ chlorinatæ* (U. S. P.)

Potassium Chlorate—*Potassii chloras* (U. S. P.)— KClO_3 —122.5—is prepared: (1) by passing Cl through a solution of KOH ; (2) by passing Cl over a mixture of milk of lime and KCl , heated to 60° ; (3) by electrolysis of KCl . By electrolytic action the KCl is split into its ions: $2\text{KCl}=2\text{K}+2\text{Cl}$; these, by secondary reactions with H_2O , produce KClO : $\text{K}_2+2\text{H}_2\text{O}=2\text{KOH}+\text{H}_2$, and $2\text{KOH}+\text{Cl}_2=2\text{KClO}+\text{H}_2$, and at the temperature generated, the KClO yields KClO_3 : $2\text{KClO}+\text{H}_2\text{O}=\text{KClO}_3+\text{KCl}+\text{H}_2$. It crystallizes in transparent, anhydrous plates, soluble in H_2O ; sparingly soluble in weak alcohol.

It fuses at 400° ; if further heated, it is decomposed into KCl and perchlorate, and at a still higher temperature the perchlorate is decomposed into KCl and O :



It is a valuable source of O , and a more active oxidant than KNO_3 . When mixed with readily oxidizable substances, C , S , P , sugar, tannin, resins, etc., the mixtures explode when subjected to shock. With strong H_2SO_4 it gives off Cl_2O_4 , an explosive yellow gas. It is decomposed by HNO_3 with formation of KNO_3 , KClO_4 , and liberation of Cl and O . Heated with HCl it gives off a mixture of Cl and Cl_2O_4 , the latter acting as an energetic oxidant in solutions in which it is generated.

Sulphates.—**Dipotassic sulphate**—*Potassium sulphate*— K_2SO_4 —174—occurs native; in the ash of many plants; and in solution in mineral waters. It may be prepared by the action of sulphuric acid on potassium carbonate:



It crystallizes in right rhombic prisms; hard; permanent in air; salt and bitter in taste; soluble in H_2O .

Monopotassic Sulphate.—*Hydropotassic sulphate*—*Acid sulphate*— KHSO_4 —136—is formed as a by-product in the manufacture of HNO_3 . When heated it loses H_2O , and is converted into the **pyro-sulphate**, $\text{K}_2\text{S}_2\text{O}_7$, which, at a higher temperature, is decomposed into K_2SO_4 and SO_3 .

Dipotassic Sulphite—*Potassic sulphite*— K_2SO_3 —158—is formed by saturating solution of K_2CO_3 with SO_2 , and evaporating over H_2SO_4 . It crystallizes in oblique rhombohedra; soluble in H_2O . Its solution absorbs O from the air, with formation of K_2SO_4 .

Potassium Dichromate—*Bichromate of potassium*— $\text{K}_2\text{Cr}_2\text{O}_7$ —294—is formed by heating a mixture of *chrome iron ore* with KNO_3 , or K_2CO_3 in air; extracting with H_2O ; neutralizing with dilute H_2SO_4 ; and evaporating. It forms large, reddish-orange colored prismatic crystals; soluble in H_2O ; fuses below redness, and at a higher temperature is decomposed into O, potassium chromate, and chromic oxide. Heated with HCl , it gives off Cl.

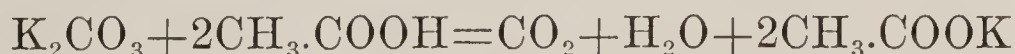
Potassium Permanganate—*Potassii permanganas* (U. S. P.)— KMnO_4 —158—is obtained by boiling a solution of potassium manganate with water:



It crystallizes in dark prisms, almost black, with greenish reflections, which, yield a red powder when broken. Soluble in H_2O , communicating to it a red color, even in very dilute solution. It is a most valuable oxidizing agent. With organic matter its solution is turned to green, by the formation of the manganate, or deposits the brown sesquioxide of manganese, according to the nature of the organic substance. In some instances the reaction takes place best in the cold, in others under the influence of heat; in some better in acid solutions, in others in alkaline solutions. Mineral reducing agents act more rapidly. Its strong oxidizing powers render its solutions valuable as disinfectants. When used as a disinfectant it is split up as follows:



Potassium Acetate—*Potassii acetas* (U. S. P.)— CH_3COOK —110—exists in the sap of plants; and it is by its calcination that the major part of the carbonate of wood ashes is formed. It is prepared by neutralizing acetic acid with K_2CO_3 or KHCO_3 :



It forms crystalline needles, deliquescent, and very soluble in H_2O ; less soluble in alcohol. Its solutions are faintly alkaline.

Carbonates.—**Potassium Carbonate**—**Dipotassic Carbonate**—**Salt of tartar**—**Pearl ash**—*Potassii carbonas* (U. S. P.)— K_2CO_3 —

138—exists in mineral waters, and in the animal economy. It is prepared industrially, in an impure form, known as **potash** or **pearl-ash**, from wood ashes, from the molasses of beet sugar, and from the native Strassfurt chloride. It is obtained pure by decomposing the monopotassic salt, purified by several recrystallizations, by heat:



or by calcining a potassium salt of an organic acid. Thus cream of tartar, mixed with nitre and heated to redness, yields a black mixture of C and K_2CO_3 , called **black flux**; on extracting which with H_2O , a pure carbonate, known as **salt of tartar**, is dissolved.

Anhydrous, it is a white, granular, deliquescent, very soluble powder. At low temperatures it crystallizes with 2Aq. Its solution is alkaline.

Monopotassic Carbonate—*Hydropotassic carbonate*—**Potassium bicarbonate**—**Potassii bicarbonas** (U. S. P)— HKCO_3 —100—is obtained by dissolving K_2CO_3 in H_2O , and saturating the solution with CO_2 :

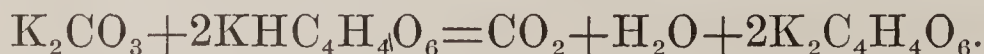


It crystallizes in oblique rhombic prisms, much less soluble than the carbonate. In solution, it is gradually converted into the dipotassic salt when heated, when brought into a vacuum, or when treated with an inert gas. The solutions are alkaline in reaction and in taste, but are not caustic.

The substance used in baking, under the name **salærat**, is this or the corresponding Na salt, usually the latter. Its extensive use in some parts of the country is undoubtedly in great measure the cause of the prevalence of dyspepsia. When used alone in baking, it “raises” the bread by decomposition into carbon dioxide and dipotassic (or disodic) carbonate, the latter producing disturbances of digestion by its strong alkaline reaction.

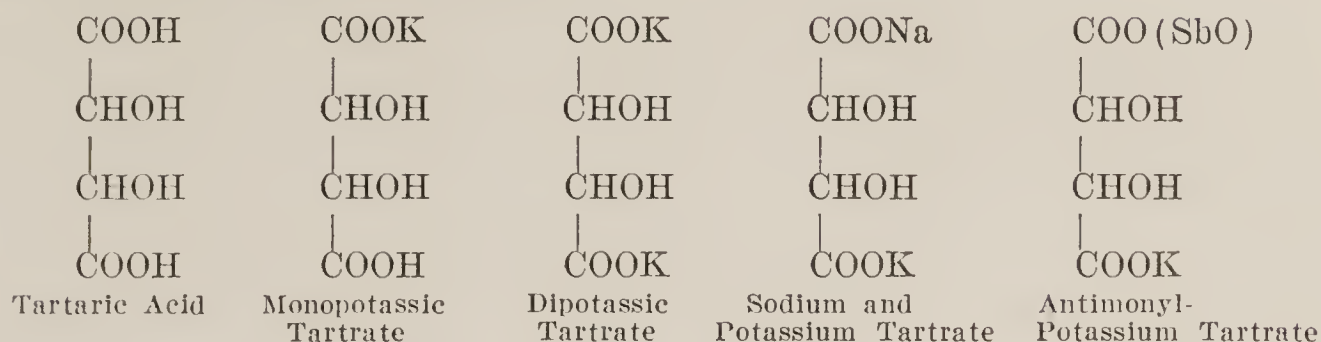
Monopotassic Oxalate— KHC_2O_4 —128—forms transparent, soluble, acid needles. It occurs along with the **quadroxalate** HKC_2O_4 , $\text{H}_2\text{C}_2\text{O}_4 + 2\text{Aq}$, in **salt of lemon** or **salt of sorrel**, used in straw bleaching, and for the removal of ink-stains, etc. It closely resembles Epsom salt in appearance, and has been fatally mistaken for it.

Tartrates.—**Dipotassic Tartrate**—**Potassium tartrate**—**Soluble tartar**—*Neutral tartrate of potash*— $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ —226—is prepared by neutralizing the hydropotassic salt with potassium carbonate:



It forms a white, crystalline powder, very soluble in H_2O , the solution being dextrogyrous, $[\alpha]_D = +28.48^\circ$; soluble in alcohol. Acids, even acetic, decompose its solution, with precipitation of the monopotassic salt.

The constitution and relation of the tartrates may be seen by a study of their graphic formulæ:



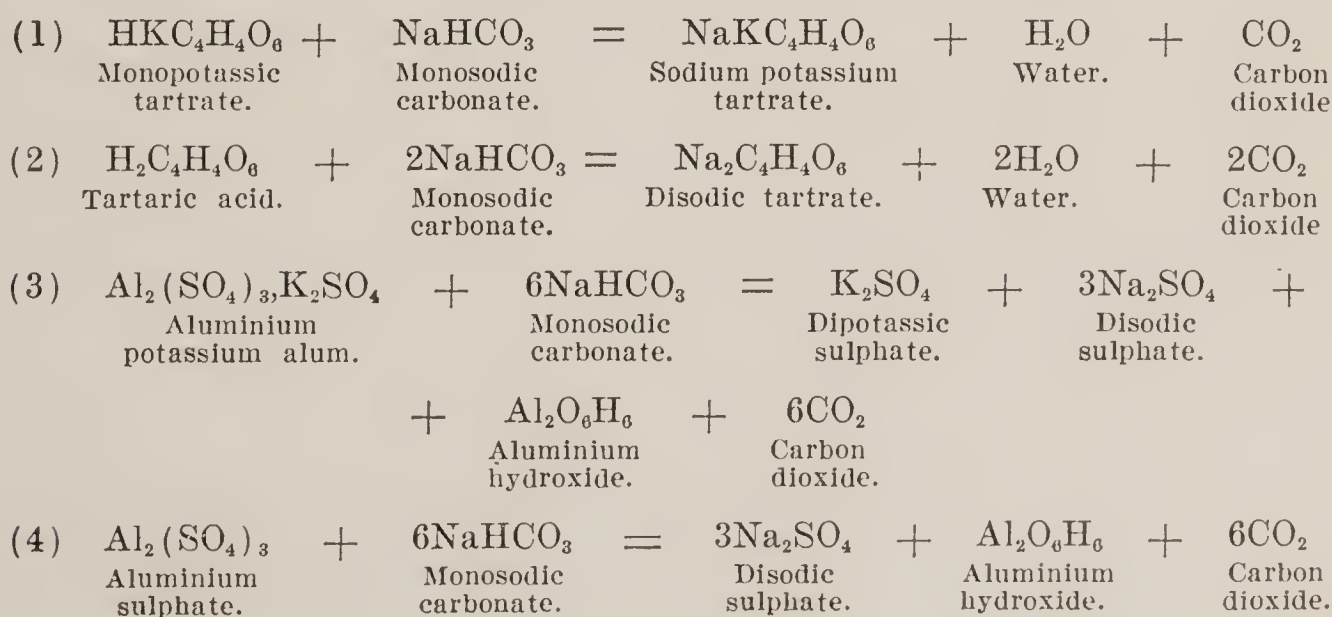
Monopotassic Tartrate—*Hydropotassic tartrate*—**Cream of tartar**—**Potassii bitartras** (U. S. P.)—**Acid potassium tartrate**—**Potassium bitartrate**— $\text{HKC}_4\text{H}_4\text{O}_6$ —188.—During the fermentation of grape juice, as the proportion of alcohol increases, crystalline crusts collect in the cask. These constitute the **crude tartar**, or **argol**, of commerce, which is composed, in great part, of monopotassic tartrate, with some calcium tartrate and coloring matter. The crude product is purified by repeated crystallization from boiling H_2O , decolorizing with animal charcoal, digesting the purified tartar with HCl at 20° , washing with cold H_2O , and crystallizing from hot H_2O .

It crystallizes in hard, opaque (translucent when pure), rhombic prisms, which have an acidulous taste, and are very sparingly soluble in H_2O , still less soluble in alcohol. Its solution is acid, and dissolves many metallic oxides with formation of double tartrates. When boiled with antimony trioxide, it forms tartar emetic.

It is used in the household, combined with monosodic carbonate, in baking, the two substances reacting upon each other to form Rochelle salt, with liberation of carbon dioxide.

Baking Powders are now largely used as substitutes for yeast to “raise” biscuits, cakes, etc. Their action is based upon the decomposition of HNaCO_3 by some salt having an acid reaction, or by a weak acid. In addition to the bicarbonate and flour, or cornstarch (added to render the bulk convenient to handle and to diminish the rapidity of the reaction), they contain cream of tartar, tartaric acid, alum, or acid phosphates.

Some of the reactions by which the CO_2 may be liberated are:



Sodium Potassium Tartrate—Rochelle salt—Potassii et sodii tartras (U. S. P.)— $\text{NaKC}_4\text{H}_4\text{O}_6 + 4\text{Aq} - 210 + 72$ —is prepared by saturating monopotassic tartrate with disodic carbonate. It crystallizes in large, transparent prisms, which effloresce superficially in dry air and attract moisture in damp air. It fuses at $70^\circ - 80^\circ$, and loses 3Aq at 100° . It is soluble in 1.4 parts of cold H_2O .

Potassium Antimonyl Tartrate—*Tartrated antimony*—Tartar emetic—Antimonii et potassii tartras (U. S. P.)— $(\text{SbO})\text{KC}_4\text{H}_2\text{O}_6 + \frac{1}{2}\text{Aq} - 331.6$ —is prepared by boiling a mixture of 3 pts. Sb_2O_3 and 4 pts. $\text{HKC}_4\text{H}_4\text{O}_6$ in H_2O for an hour, filtering, and allowing to crystallize:



It crystallizes in transparent, soluble, right rhombic octahedra, which turn white in air. Its solutions are acid in reaction, have a nauseating metallic taste, and are precipitated by alcohol. The crystals contain $\frac{1}{2}$ Aq, which they lose entirely at 100° , and, partially by exposure to air. It is decomposed by the alkalies, alkaline earths, and alkaline carbonates, with precipitation of Sb_2O_3 . The precipitate is redissolved by excess of soda or potash, or by tartaric acid. HCl , H_2SO_4 and HNO_3 precipitate corresponding antimonyl compounds from solutions of tartar emetic. It converts mercuric into mercurous chloride. It forms double tartrates with the tartrates of the alkaloids.

Potassium Cyanide.—KCN—65—is obtained by heating a mixture of potassium ferrocyanide and dry K_2CO_3 , as long as effervescence continues; decanting and crystallizing:



It is usually met with in dull, white, amorphous masses. Odorless when dry, it has the odor of hydrocyanic acid when moist. It is deliquescent, and very soluble in H_2O ; almost insoluble in alcohol. Its solution is acrid and bitter in taste, with an after-taste of hydrocyanic acid. It is very readily oxidized to the cyanate, a property which renders it valuable as a reducing agent. Solutions of KCN dissolve I , AgCl , the cyanides of Ag and Au , and many metallic oxides.

It is actively poisonous, and produces its effects by decomposition and liberation of hydrocyanic acid (*q. v.*).

Potassium Ferrocyanide—Yellow prussiate of potash— $\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{Aq} - 368 + 54$ —This salt, the source of the other cyanogen compounds, is manufactured by adding nitrogenous organic matter (blood, bones, hoofs, leather, etc.) and iron to K_2CO_3 in fusion; or by other processes in which the N is obtained from the residues of the purification of coal gas, from atmospheric air, or from ammoniacal compounds.

It forms soft, flexible, lemon-yellow crystals, permanent in air at ordinary temperatures. They begin to lose Aq at 60° , and become anhydrous at 100° . Soluble in H_2O ; insoluble in alcohol, which precipitates it from its aqueous solution. When calcined with KOH or K_2CO_3 potassium cyanide and cyanate

are formed, and Fe is precipitated. Heated with dilute H_2SO_4 , it yields an insoluble white or blue salt, potassium sulphate, and hydrocyanic acid. Its solutions form, with those of many of the metallic salts, insoluble ferrocyanides; those of Zn, Pb, and Ag are white, cupric ferrocyanide is mahogany-colored, ferrous ferrocyanide is bluish white, ferric ferrocyanide, **Prussian blue**, is dark blue. Blue ink is a solution of Prussian blue in a solution of oxalic acid.

Potassium Ferricyanide—Red prussiate of potash— $\text{K}_3\text{Fe}(\text{CN})_6$ —329—is prepared by acting upon the ferrocyanide with chlorine; or, better, by heating the white residue of the action of H_2SO_4 upon potassium ferrocyanide, in the preparation of hydrocyanic acid, with a mixture of 1 vol. HNO_3 and 20 vols. H_2O ; the *blue* product is digested with H_2O , and potassium ferrocyanide, the solution filtered and evaporated. It forms red, oblique rhombic prisms, almost insoluble in alcohol. With solutions of ferrous salts it gives dark blue precipitate, **Turnbull's blue**.

Analytical Characters.—(1) Platinic chloride, in presence of HCl : yellow ppt., K_2PtCl_6 ; crystalline if slowly formed; sparingly soluble in H_2O , much less so in alcohol. (2) Tartaric acid in not too dilute solution: white ppt.; soluble in alkalis and in concentrated acids. (3) Hydrofluosilicic acid: translucent, gelatinous ppt.; forms slowly; soluble in strong alkalis. (4) Perchloric acid: white ppt.; sparingly soluble in H_2O ; insoluble in alcohol. (5) Phosphomolybdic acid: white ppt.; forms slowly. (6) Colors the Bunsen flame violet (the color is only observable through blue glass in the presence of Na), and exhibits a spectrum of two bright lines: $\lambda = 7860$ and 4045 (Fig. 16, No. 3, p. 150).

Action of the Sodium and Potassium Compounds on the Economy.—The hydroxides of Na and K, and in a less degree the carbonates, disintegrate animal tissues, dead or living, with which they come in contact, and, by virtue of this action, act as powerful caustics upon a living tissue. Upon the skin, they produce a soapy feeling, and in the mouth a soapy taste. Like the acids, they cause death, either immediately, by corrosion or perforation of the stomach; or, secondarily, after weeks or months, by closure of one or both openings of the stomach, due to thickening, consequent upon inflammation.

The *treatment* consists in the neutralization of the alkali by an acid, dilute vinegar. Neutral. Neutral oils and milk are of service, more by reason of their emollient action than for any power they have to neutralize the alkali, by the formation of a soap, at the temperature of the body.

The other compounds of Na, if the acid is not poisonous, are without deleterious action, unless taken in excessive quantity. Common salt has produced paralysis and death in a dose of half a pound. The neutral salts of K, on the contrary, are by no means without true poisonous action when taken internally, or injected subcutaneously, in sufficient quantities; causing dyspnea, convulsions, arrest of the heart's action, and death. In the adult human subject, death has followed the ingestion of doses of 15–30 gms. of the nitrate, in several instances; doses of 8–60 gms. of the sulphate have also proved fatal.

CÆSIUM AND RUBIDIUM.

Cæsium—*Symbol* = Cs—*Atomic weight* = 133—(*International* = 132.81; and **Rubidium**—*Symbol* = Rb—*Atomic weight* = 85—*International* = 85.45); are two rare elements, discovered in 1860 by Kirch-

off and Bunsen while examining spectroscopically the ash of a spring water. They exist in very small quantity in *lepidolite*. They combine with O and decompose H_2O even more energetically than does K, forming strongly alkaline hydroxides.

SILVER.

Symbol=Ag (*Argentum*)—*Atomic weight*=108—(*International* =107.88)—*Molecular weight*=216—*Sp. gr.*=10.4–10.54.

Although silver is usually classed with the “noble metals,” it differs from Au and Pt widely in its chemical characters, in which it more closely resembles the alkaline metals.

Silver occurs free in nature, also in combination as the sulphide or chloride; it is frequently contained in other sulphides, notably those of Sb, Pb, and Cu.

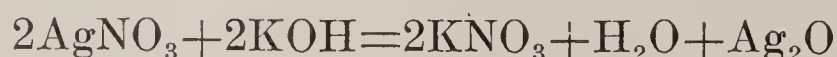
When pure Ag is required, coin silver is dissolved in HNO_3 and the diluted solution precipitated with HCl. The silver chloride is washed, until the washings no longer precipitate with silver nitrate; and reduced, either (1) by suspending it in dilute H_2SO_4 in a platinum basin, with a bar of pure Zn, and washing thoroughly, after complete reduction; or (2) by mixing it with chalk and charcoal (AgCl, 100 parts; C, 5 parts; $CaCO_3$, 70 parts), and gradually introducing the mixture into a red-hot crucible.

Silver is a white metal; very malleable and ductile; the best known conductor of heat and electricity. It is not acted on by pure air, but is blackened in air containing a trace of H_2S . It combines directly with Cl, Br, I, S, P, and As. Hot H_2SO_4 dissolves it as sulphate, and HNO_3 as nitrate. The caustic alkalies do not affect it. It alloys readily with many metals; its alloy with Cu is harder than the pure metal.

Silver seems to exist in a number of allotropic modifications, besides that in which it is ordinarily met with. In one of these it is brilliant, metallic, bluish green in color, and dissolves in H_2O , forming a deep red solution; in another it has the color of burnished gold, when dry; and in still another it has also a bluish green color, but is insoluble in water. Very dilute mineral acids immediately convert these modifications into normal gray silver, without evolution of any gas.

Oxides.—Three oxides of silver are known: Ag_4O , Ag_2O , and Ag_2O_2 .

Silver Monoxide—Argenti oxidum—(U. S. P.)— Ag_2O —232—formed by precipitating a solution of silver nitrate with potash:



It is a brownish powder; faintly alkaline and very slightly

soluble in H_2O ; strongly basic. It readily gives up its oxygen. On contact with ammonium hydroxide it forms a fulminating powder.

Silver Chloride— AgCl —143.5—formed when HCl or a chloride is added to a solution containing silver. It is white; turns violet and black in sunlight; volatilizes at 260° ; sparingly soluble in HCl ; soluble in solutions of the alkaline chlorides, thiosulphates, and cyanides, and in ammonium hydroxide. It crystallizes in octahedra on exposure of its ammoniacal solution.

Silver Bromide— AgBr —and **Iodide**— AgI —are yellowish precipitates, formed by decomposing silver nitrate with potassium bromide and iodide. The former is very sparingly soluble in ammonium hydroxide, the latter is insoluble.

Silver Nitrate—**Argenti nitras** (U. S. P.)— AgNO_3 —170—is prepared by dissolving Ag in HNO_3 , evaporating, fusing, and recrystallizing. It crystallizes in anhydrous, right rhombic plates; soluble in H_2O . The solutions are colorless and neutral. In the presence of organic matter it turns black in sunlight.

The salt, fused and cast into cylindrical moulds, constitutes **lunar caustic**, **lapis infernalis**; **argenti nitras fusus** (U. S. P.). If, during fusion, the temperature is raised too high, it is converted into nitrite, O , and Ag ; and if sufficiently heated leaves pure Ag .

Dry Cl and I decompose it, with liberation of anhydrous HNO_3 . It absorbs NH_3 , to form a white solid, $\text{AgNO}_3 \cdot 3\text{NH}_3$, which gives up its NH_3 when heated. Its solution is decomposed very slowly by H , with deposition of Ag .

Analytical Characters.—(1) Hydrochloric acid: white flocculent ppt.; soluble in NH_4OH ; insoluble in HNO_3 . (2) Potash or soda: brown ppt.; insoluble in excess; soluble in NH_4OH . (3) Ammonium hydroxide, from neutral solutions: brown ppt.; soluble in excess. (4) Hydrogen sulphide or ammonium sulphhydrate: black ppt. insoluble in NH_4HS . (5) Potassium bromide: yellowish white ppt.; insoluble in acids, if not in great excess; soluble in NH_4OH . (6) Potassium iodide: same as KBr , but the ppt. is less soluble in NH_4OH .

Action on the Economy.—Silver nitrate acts both locally as a corrosive, and systemically as a true poison. Its local action is due to its decomposition, by contact with organic substances, resulting in the separation of elementary Ag , whose deposition causes a black stain, and liberation of free HNO_3 , which acts as a caustic. When absorbed, it causes nervous symptoms, referable to its poisonous action. The blue coloration of the skin, observed in those to whom it is administered for some time, is due to the reduction of the metal, under the combined influence of light and organic matter; especially of the latter, as the darkening is observed, although it is less intense, in internal organs.

In acute poisoning by silver nitrate, sodium chloride or white of egg should be given; and, if the case is seen before the symptoms of corrosion are far advanced, emetics.

AMMONIUM COMPOUNDS.

The Ammonium Theory.—Although neither the radical ammonium, NH_4 , nor the molecule $(\text{NH}_4)_2$ has ever been isolated, the existence of the radical in the ammoniacal compounds is almost uni-

versally admitted. The ammonium hypothesis is based chiefly upon the following facts: (1) the close resemblance of the ammoniacal salts to those of K and Na; (2) when ammonia gas and an acid gas come together, they unite, *without liberation of hydrogen*, to form an ammonium salt; (3) when solutions of the ammoniacal salts are subjected to electrolysis, a mixture, having the composition $\text{NH}_3 + \text{H}$ is given off at the negative pole; (4) amalgam of sodium, in contact with a concentrated solution of ammonium chloride, increases much in volume, and is converted into a light, soft mass, having the luster of mercury. This **ammonium amalgam** is decomposed gradually, giving off ammonia and hydrogen in the proportion $\text{NH}_3 + \text{H}$; (5) if the gases $\text{NH}_3 + \text{H}$, given off by decomposition of the amalgam, exist there in simple solution, the liberated H would have the ordinary properties of that element. If, on the other hand, they exist in combination, the H would exhibit the more energetic affinities of an element in the nascent state. The hydrogen so liberated is in the nascent state.

Ammonium Hydroxide—Caustic ammonia— NH_4OH —35—has never been isolated, probably owing to its tendency to decomposition; $\text{NH}_4\text{OH} = \text{NH}_3 + \text{H}_2\text{O}$. It is considered as existing in the so-called aqueous solutions of ammonia. These are colorless liquids; of less sp. gr. than H_2O ; strongly alkaline; and having the taste and odor of ammonia, which gas they give off on exposure to air, and more rapidly when heated. They are neutralized by acids, with elevation of temperature and formation of ammoniacal salts. The **Aqua ammoniæ** and **Aqua ammoniæ fortior** (U. S. P.) are such solutions; the former contains about 10 per cent. and the latter 28 per cent. of NH_3 .

Ammonium Hydrogen Sulphide—Ammonium Sulphydrate— N_4HS —51—is formed, in solution by saturating a solution of NH_4HO with H_2S ; or, anhydrous, by mixing equal volumes of dry NH_3 and dry H_2S .

The anhydrous compound is a colorless, transparent, volatile and soluble solid. The solution, when freshly prepared, is colorless, but soon becomes yellow from oxidation, and formation of ammonium disulphide and thiosulphate, and finally deposits sulphur.

The sulphides and hydrosulphide of ammonium are also formed during the decomposition of protein bodies, and exist in the gases formed in burial vaults, sewers, etc.

Ammonium Chloride—Sal ammoniac—Ammonii chloridum (U. S. P.)— NH_4Cl —53.5—is obtained from the ammoniacal water of gas works. It is a translucent, fibrous, elastic solid; salty in taste, neutral in reaction; volatile without fusion or decomposition; soluble in H_2O . Its solution is neutral, but loses NH_3 and becomes acid when boiled.

Ammonium chloride exists in small quantity in the gastric juice of the sheep and dog; also in the perspiration, urine, saliva and tears.

Ammonium Bromide—*Ammonii bromidum* (U. S. P.)— $(\text{NH}_4)\text{Br}$ —98—is formed either by combining NH_3 and HBr ; by decomposing ferrous bromide with NH_4OH ; or by double decomposition between KBr and $(\text{NH}_4)_2\text{SO}_4$. It is a white, granular powder, or crystallizes in large prisms, which turn yellow on exposure to air; quite soluble in H_2O ; volatile without decomposition.

Ammonium Iodide—*Ammonii iodidum* (U. S. P.)— NH_4I —145—is formed by union of equal volumes of NH_3 and HI ; or by double decomposition of KI and $(\text{NH}_4)_2\text{SO}_4$. It crystallizes in deliquescent, very soluble cubes.

Ammonium Nitrate— $(\text{NH}_4)\text{NO}_3$ —80—is prepared by neutralizing HNO_3 with ammonium hydroxide or carbonate. It crystallizes in flexible, anhydrous, six-sided prisms; very soluble in H_2O , with considerable diminution of temperature; fuses at 150° , and decomposes at 210° , with formation of nitrous oxide: $(\text{NH}_4)\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$. If the heat is suddenly applied, or allowed to surpass 250° , NH_2 , NO , and N_2O are formed. When fused it is an active oxidant.

Sulphates.—**Diammonic Sulphate**—*Ammonic sulphate*— $(\text{NH}_4)_2\text{SO}_4$ —132—is obtained by collecting the distillate from a mixture of ammoniacal gas liquor and lime in H_2SO_4 . It forms anhydrous, soluble, rhombic crystals; fuses at 150° , and is decomposed at 200° into NH_3 and $\text{H}(\text{NH}_4)\text{SO}_4$.

Monoammonic Sulphate—*Hydroammonic sulphate*—*Bismuth of ammonia*— $\text{H}(\text{NH}_4)\text{SO}_4$ —115—is formed by the action of H_2SO_4 on $(\text{NH}_4)_2\text{SO}_4$. It crystallizes in right rhombic prisms, soluble in H_2O and in alcohol.

Ammonium Acetate— $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$ —77—is formed by saturating acetic acid with NH_3 , or with ammonium carbonate. It is a white, odorless, very soluble solid; fuses at 86° , and gives off NH_3 ; then acetic acid, and finally acetamide. **Liquor ammonii acetatis** (U. S. P.) = **Spirit of Minderus** is an aqueous solution of this salt, containing not less than 7 per cent. of ammonium acetate.

Ammonium Sesquicarbonate—**Ammonium Carbonate**—**Sal volatile**—**Preston salts**—*Ammonii carbonas* (U. S. P.) ;— $\text{NH}_4\text{HCO}_3 + \text{NH}_4\text{CO}_2\text{NH}_2$ —157—is prepared by heating a mixture of NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ and chalk, and condensing the product. It crystallizes in rhombic prisms; has an ammoniacal odor and an alkaline reaction; soluble in H_2O . By exposure to air or by heating its solution, it is decomposed into H_2O , NH_3 , and $\text{H}(\text{NH}_4)\text{CO}_3$. It is not a pure salt, but a mixture of monoammonium carbonate and ammonium carbamate.

Analytical Characters.—(1) Entirely volatile at high temperatures. (2) Heated with KOH , the ammoniacal compounds give off NH_3 , recognizable: (a) by changing moist red litmus to blue; (b) by its odor; (c) by forming a white cloud on contact with a glass rod moistened with HCl . (3) With platinic chloride: a yellow, crystalline ppt.

Action on the Economy.—Solutions of the hydroxide and carbonate act upon animal tissues in the same way as the corresponding Na and K compounds. They, moreover, disengage NH_3 , which causes intense dyspnea, irritation of the air-passages, and suffocation.

The *treatment* indicated is the neutralization of the alkali by a dilute acid. Usually the vapor of acetic acid or of dilute HCl must be administered by inhalation.

II. THALLIUM GROUP.

THALLIUM.

Symbol=Tl—*Atomic weight*=204—(*International*=204.00)—*Sp. gr.*=11.8–11.9.

A rare element, first obtained from the deposits in flues of sulphuric acid factories, in which pyrites from the Hartz were used. It resembles Pb in appearance and in physical properties, but differs entirely from that element in its chemical characters. It resembles Au in being univalent and trivalent, but differs from it, and resembles the alkali metals in being readily oxidized, in forming alums, and in forming no acid hydrate. It differs from the alkali metals in the thallic compounds, which contain Tl^{'''}. It is characterized spectroscopically by a bright green line— $\lambda=5349$.

III. CALCIUM GROUP.

Metals of the Alkaline Earths.

CALCIUM—STRONTIUM—BARIUM.

The members of this group are bivalent in all their compounds; each forms two oxides: MO and MO₂; each forms a hydroxide, having well-marked basic characters.

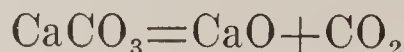
CALCIUM.

Symbol=Ca—*Atomic weight*=40—(*International*=40.07)—*Molecular weight*=80—*Sp. gr.*=1.984.

Occurs only in combination, as limestone, marble, chalk (CaCO₃), gypsum, selenite, alabaster (CaSO₄), and many other minerals. In bones, egg-shells, oyster-shells, etc., as Ca₃(PO₄)₂ and CaCO₃, and in many vegetable structures.

The element is obtained by electrolysis of fused CaCl₂, or by heating CaI₂ with Na. It is a hard, yellow, very ductile, and malleable metal, fusible at a red heat; not sensibly volatile. In dry air it is not altered, but is converted into CaH₂O₂ in damp air; decomposes H₂O; burns when heated in air.

Calcium Oxide—Quick Lime—Lime—Calx (U. S. P.)—CaO—56—is prepared by heating a native carbonate (limestone); or, when required pure, by heating a carbonate, prepared by precipitation:

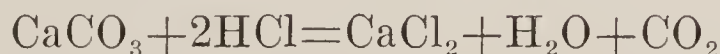


It occurs in white or grayish, amorphous masses; odorless; alkaline, caustic; almost infusible; sp. gr. 2.3. With H_2O it gives off great heat and is converted into the hydroxide (**slaking**). In air it becomes **air-slaked**, falling into a white powder, having the composition CaCO_3 , CaH_2O_2 .

Calcium Hydroxide—Calcium Hydrate—Slaked lime— $\text{Ca}(\text{OH})_2$ —74—is formed by the action of H_2O on CaO . If the quantity of H_2O used be one-third that of the oxide, the hydroxide remains as a dry, white, odorless powder; alkaline in taste and reaction; more soluble in cold than in hot H_2O . If the quantity of H_2O is greater, a creamy or milky liquid remains, **cream**, or **milk of lime**; a solution holding an excess in suspension. With a sufficient quantity of H_2O the hydroxide is dissolved to a clear solution, which is **lime water—Liquor calcis** (U. S. P.). The solubility of $\text{Ca}(\text{OH})_2$ is diminished by the presence of alkalies, and is increased by sugar or mannite. Solutions of $\text{Ca}(\text{OH})_2$ absorb CO_2 with formation of a white deposit of CaCO_3 .

Calcium Carbide— CaC_2 —is formed by the action of a very high temperature upon a mixture of quick lime and carbon. It is an amorphous grayish substance, which is decomposed by water, yielding acetylene gas: $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$. One kilo. CaC_2 yields 440 litres C_2H_2 .

Calcium Chloride—Calcii chloridum (U. S. P.)— CaCl_2 —111—is obtained by dissolving marble in HCl :



It is bitter, deliquescent, very soluble in H_2O ; crystallizes with 6Aq, which it loses when fused, leaving a white, amorphous mass, used as a drying agent.

Chlorinated Lime—Chloride of Lime—Bleaching powder—Calx chlorinata (U. S. P.)—is a white or yellowish, hygroscopic powder, prepared by passing Cl over $\text{Ca}(\text{OH})_2$, maintained in excess. It is bitter and acrid in taste; soluble in cold H_2O ; decomposed by boiling H_2O , and by the weakest acids, with liberation of Cl . It is decomposed by CO_2 , with formation of CaCO_3 , and liberation of hypochlorous acid, if it be moist; or of Cl , if it be dry. A valuable disinfectant. The “available chlorine” is the amount liberated by acids, and should be not less than 30 per cent.

Bleaching powder was formerly considered as a mixture of calcium chloride and hypochlorite, formed by the reaction: $2\text{CaO} + 2\text{Cl}_2 = \text{CaCl}_2 + \text{Ca}(\text{ClO})_2$, but it is more probable that it is a definite compound having the formula $\text{CaCl}(\text{OCl})$, which is decomposed by H_2O into a mixture of CaCl_2 and $\text{Ca}(\text{ClO})_2$; and by dilute HNO_3 or H_2SO_4 with formation of HClO .

Calcium Sulphate— CaSO_4 —136—occurs in nature as *anhydrite*; and with 2Aq in *gypsum*, *alabaster*, *selenite*; and in solution in

natural waters. **Terra alba** is ground gypsum. It crystallizes with 2Aq in right rhombic prisms; sparingly soluble in H_2O , more soluble in H_2O containing free acids or chlorides. When the hydrated salt (gypsum) is heated to 80° , or, more rapidly, between 120° – 130° , it loses its Aq and is converted into a white, opaque mass, which, when ground, is **plaster of Paris**.

The **setting** of plaster when mixed with H_2O , is due to the conversion of the anhydrous into the crystalline, hydrated salt. The ordinary plastering should never be used in hospitals, as, by reason of its irregularities and porosity, it soon becomes saturated with septic germs, and cannot be thoroughly purified by disinfectants. Plaster surfaces may, however, be rendered dense, and be highly polished, so as to be smooth and impermeable, by adding glue and alum, or an alkaline silicate to the water used in mixing.

Calcium Phosphate—Tricalcic Phosphate—Tribasic or neutral phosphate—Bone Phosphate—Phosphate of Lime— $\text{Ca}_3(\text{PO}_4)_2$ —310—occurs in nature, in soils, guano, *coprolites*, phosphorite, in all plants, and in every animal tissue and fluid. It is obtained by dissolving bone-ash in HCl , filtering, and precipitating with NH_4OH ; or by double decomposition between CaCl_2 and an alkaline phosphate. When freshly precipitated it is gelatinous; when dry, a light, white, amorphous powder; almost insoluble in pure H_2O ; soluble to a slight extent in H_2O containing ammoniacal salts, or NaCl or NaNO_3 ; readily soluble in dilute acids, even in H_2O charged with carbonic acid. It is decomposed by H_2SO_4 into CaSO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$. **Bone-ash** is an impure form of $\text{Ca}_3(\text{PO}_4)_2$, obtained by calcining bones, and used in the manufacture of P and of superphosphate.

Calcium Carbonate— CaCO_3 —100—the most abundant of the natural compounds of Ca, exists as *limestone*, *calcspar*, *chalk*, *marble*, *Iceland spar*, and *arragonite*; and forms the basis of corals, shells of crustacea and of molluscs, etc. **Otoliths**, which occur in the internal ear, parotid calculi, and sometimes vesical calculi consist of CaCO_3 .

Precipitated chalk—Calcii carbonas præcipitatus (U. S. P.)—is prepared by precipitating a solution of CaCl_2 with one of Na_2CO_3 . **Prepared chalk—Creta præparata** (U. S. P.)—is native chalk, purified by grinding with H_2O , diluting, allowing the coarser particles to subside, decanting the still turbid liquid, collecting and drying the finer particles. Such a process is known as **elutriation** or **levigation**.

It is a white powder, almost insoluble in pure H_2O ; much more soluble in H_2O containing carbonic acid, the solution being regarded as containing **monocalcic carbonate**, $\text{H}_2\text{Ca}(\text{CO}_3)_2$. At a red heat it yields CO_2 and CaO . It is decomposed by acids with liberation of CO_2 .

Calcium Oxalate—Oxalate of lime— CaC_2O_4 —128—exists in the sap of many plants, in human urine, and in **mulberry calculi**, and is

formed as a white, crystalline precipitate, by double decomposition, between a Ca salt and an alkaline oxalate. It is insoluble in H_2O , acetic acid, or NH_4OH ; soluble in the mineral acids and in solution of H_2NaPO_4 .

Analytical Characters.—(1) Ammonium sulphhydrate: nothing, unless the Ca salt be the phosphate, oxalate or fluoride, when it forms a white ppt. (2) Alkaline carbonates: white ppt.; not prevented by the presence of ammoniacal salts. (3) Ammonium oxalate: white ppt., insoluble in acetic acid; soluble in HCl or HNO_3 . (4) Sulphuric acid: white ppt., either immediately or on dilution with three volumes of alcohol; very sparingly soluble in H_2O , insoluble in alcohol; soluble in sodium thiosulphate solution. (5) Sodium tungstate: dense white ppt., even from dilute solutions. (6) Colors the flame of the Bunsen burner reddish-yellow, and exhibits a spectrum of a number of bright bands, the most prominent of which are: $\lambda = 6265, 6202, 6181, 6044, 5982, 5933, 5543, \text{ and } 5517$.

STRONTIUM.

Symbol = Sr—*Atomic weight* = 87.5—(*International* = 87.63)—*Sp. gr.* = 2.54.

An element not as abundant as Ba, occurring principally in the minerals *strontianite* (SrCO_3) and *celestine* (SrSO_4). Its compounds resemble those of Ca and Ba. Its nitrate is used in making red fire. The bromide, iodide, and the salicylate are official in the U. S. P.

Analytical Characters.—(1) Behaves like Ba with alkaline carbonates and Na_2HPO_4 . (2) Calcium sulphate: a white ppt., which forms slowly; accelerated by addition of alcohol. (3) The Sr compounds color the Bunsen flame red, or, as observed through blue glass, purple or rose color. The Sr flame gives a spectrum of many bands, of which the most prominent are: $\lambda = 6694, 6664, 6059, 6031, 4607$.

BARIUM.

Symbol = Ba—*Atomic weight* = 137—(*International* = 137.37)—*Molecular weight* = 274—*Sp. gr.* = 4.0.

Occurs only in combination, principally as *heavy spar* (BaSO_4) and *witherite* (BaCO_3). It is a pale yellow, malleable metal, quickly oxidized in air, and decomposing H_2O at ordinary temperatures.

Oxides.—**Barium Monoxide**—**Baryta**— BaO —153—is prepared by calcining the nitrate:



It is a grayish-white or white, amorphous, caustic solid. In air it absorbs moisture and CO_2 , and combines with H_2O as does CaO .

Barium Dioxide— BaO_2 —169—is prepared by heating the monoxide in O . It is a grayish-white, amorphous solid. Heated in air it is decomposed: $\text{BaO}_2 = \text{BaO} + \text{O}$. Aqueous acids dissolve it with formation of a barytic salt and H_2O_2 .

Barium Hydroxide— $\text{Ba}(\text{OH})_2$ —171—is prepared by the action of H_2O on BaO . It is a white, amorphous solid, soluble in H_2O . Its aqueous solution, **baryta water**, is alkaline, and absorbs CO_2 , with formation of a white deposit of BaCO_3 .

Barium Chloride— $\text{BaCl}_2 + 2 \text{ Aq}$ —208+36—is obtained by treating BaS or BaCO_3 with HCl . It crystallizes in prismatic plates, permanent in air, soluble in H_2O .

Barium Nitrate— $\text{Ba}(\text{NO}_3)_2$ —261—is prepared by neutralizing HNO_3 with BaCO_3 . It forms octahedral crystals, soluble in H_2O .

Barium Sulphate— BaSO_4 —233—occurs in nature as *heavy spar*, and is formed as an amorphous, white powder, insoluble in acids, by double decomposition between a Ba salt and a sulphate in solution. It is insoluble in H_2O and in acids. It is used as a pigment, **permanent white**.

Barium Carbonate— BaCO_3 —197—occurs in nature as *witherite*, and is formed by double decomposition between a Ba salt and a carbonate in alkaline solution. It is a heavy, amorphous, white powder, insoluble in H_2O , soluble with effervescence in acids.

Analytical Characters.—(1) Alkaline carbonates: white ppt., in alkaline solution. (2) Sulphuric acid, or calcium sulphate: white ppt., insoluble in acids. (3) Sodium phosphate: white ppt., soluble in HNO_3 . (4) Colors the Bunsen flame greenish-yellow, and exhibits a spectrum of several lines, the most prominent of which are: $\lambda = 6108, 6044, 5881, 5536$.

Action on the Economy.—The oxides and hydroxide act as corrosives, by virtue of their alkalinity, and also as true poisons. All soluble compounds of Ba, and those which are readily converted into soluble compounds in the stomach, are actively poisonous. Soluble sulphides, followed by emetics, are indicated as antidotes. The sulphate, notwithstanding its insolubility in water, is poisonous to some animals.

IV. MAGNESIUM GROUP.

MAGNESIUM—ZINC—CADMIUM.

Each of these elements forms a single oxide—a corresponding basic hydroxide, and a series of salts in which its atoms are bivalent.

The existence of potassium zincate, ZnO_2K_2 , obtainable by the action of zinc hydroxide and potassium hydroxide upon each other: $\text{Zn}(\text{OH})_2 + 2\text{KOH} = \text{ZnO}_2\text{K}_2 + 2\text{H}_2\text{O}$ would seem to require the transferral of zinc to the amphoteric class; the $\text{Zn}(\text{OH})_2$ in the above reaction fulfilling the requirements of the second definition of acids (see p. 178). Potassium zincate should, however, be considered rather

as a double oxide of zinc and potassium: ZnOK_2O or Zn.OK.OK , than as a true salt for the following reasons: (1) It is also produced by the reaction: $\text{Zn} + 2\text{KOH} = \text{ZnO}_2\text{K}_2 + \text{H}_2$, in which, if ZnO_2K_2 be a salt, KOH , the most distinctly basic substance known, must be considered to be an acid. (2) In the electrolysis of ZnO_2K_2 the Zn and K go to the negative pole, and the O to the positive, while in the electrolysis of true ternary salts, such as K_2SO_4 , the oxygen accompanies the other electro-negative element to the positive pole, the metal going alone to the negative. Moreover, the zincates are unstable bodies, and the most prominent function of Zn(OH)_2 is that of a base, as in the reaction $\text{Zn(OH)}_2 + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + 2\text{HO}_2$. (See Aluminium, p. 178.)

MAGNESIUM.

Symbol = Mg — *Atomic weight* = 24 — (*International* = 24.32) — *Molecular weight* = 48 — *Sp. gr* = 1.75.

Occurs as carbonate in *dolomite* or *magnesium limestone*, and as silicate in *mica*, *asbestos*, *soapstone*, *meerschau*, *tal*, and in other minerals. It also accompanies Ca in the forms in which it is found in the animal and vegetable worlds.

It is prepared by heating its chloride with Na, or by electrolysis of the fused chloride. It is a hard, light, malleable, ductile, white metal. It burns with great brilliancy when heated in air (magnesium light), but may be distilled in H. The flash light used by photographers is a mixture of powdered Mg with an oxidizing agent, KClO_3 or KNO_3 . It decomposes vapor of H_2O when heated; reduces CO_2 with the aid of heat, and combines directly with Cl, S, P, As and N. It dissolves in dilute acids, but is not affected by alkaline solutions.

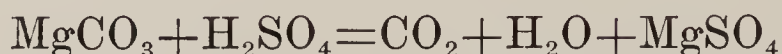
Magnesium Oxide—**Calcined magnesia**—**Magnesii oxidum**—**Magnesia** (U. S. P.)— MgO —40—is obtained by calcining the carbonates, hydroxide, or nitrate. It is a light, bulky, tasteless, odorless, amorphous, white powder; alkaline in reaction; almost insoluble in H_2O ; readily soluble without effervescence in acids.

Magnesium Hydroxide— Mg(OH)_2 —58—occurs in nature, and is formed when a solution of a Mg salt is precipitated with excess of NaOH in absence of ammoniacal salts. It is a heavy, white powder, insoluble in H_2O , absorbs CO_2 .

Magnesium Chloride— MgCl_2 —95—is formed when MgO or MgCO_3 is dissolved in HCl . It is an exceedingly deliquescent, soluble substance, which is decomposed into HCl and MgO when its aqueous solutions are evaporated to dryness. Like all the soluble Mg compounds it is bitter in taste, and accompanies the sulphate and bicarbonate in the *bitter waters*.

Magnesium Sulphate—**Epsom salt**—*Seidlitz salt*—**Magnesii sul-**

phas (U. S. P.)— $\text{MgSO}_4 + 7\text{Aq}$ —120+126—exists in solution in sea water and in the waters of many mineral springs, especially those known as **bitter waters**. It is formed by the action of H_2SO_4 on MgCO_3 :



It crystallizes in right rhombic prisms; bitter, slightly effervescent, and quite soluble in H_2O . Heated, it fuses and gradually loses 6Aq up to 132° ; the last Aq it loses at 210° .

Phosphates.—Resemble those of Ca in their constitution and properties, and accompany them in the situations in which they occur in the animal body, but in much smaller quantity.

Magnesium also forms double phosphates, constituted by the substitution of one atom of the bivalent metal for two of the atoms of basic hydrogen, of a molecule of phosphoric acid, and of an atom of alkaline metal, or of an ammonium group, for the remaining basic hydrogen.

Ammonium-Magnesium Phosphate—Triple phosphate— $\text{Mg}(\text{NH}_4)\text{PO}_4 + 6\text{Aq}$ —137+108—is produced when an alkaline phosphate and NH_4OH are added to a solution containing Mg. When heated it is converted into **magnesium pyrophosphate**, $\text{Mg}_2\text{P}_2\text{O}_7$, in which form H_3PO_4 and Mg are usually weighed in quantitative analysis.

Carbonates.—**Magnesium Carbonate**—*Normal Magnesium carbonate*— MgCO_3 —84—exists native in *magnesite*, and, combined with CaCO_3 , in *dolomite*. It cannot be formed, like other carbonates, by decomposing a Mg salt with an alkaline carbonate, but may be obtained by passing CO_2 through H_2O holding tetramagnesian tricarbo-nate in suspension.

Tetramagnesian Tricarbonate—*Magnesia alba*—*Magnesium carbonate* (U. S. P.)— $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 + 4\text{Aq}$ —310+72—occurs in commerce in light, white cubes, composed of a powder which is amorphous, or partly crystalline. It is prepared by precipitating a solution of MgSO_4 with one of Na_2CO_3 :



If the precipitation occurs in cold, dilute solutions, very little CO_2 is given off; a light, bulky precipitate falls (the *light carbonate*), and the solution contains magnesium, probably in the form of the *bicarbonate* $\text{Mg}(\text{HCO}_3)_2$. This solution, on standing, deposits crystals of the carbonate, $\text{MgCO}_3 + 3\text{Aq}$. If hot concentrated solutions are used, and the liquid is then boiled upon the precipitate, CO_2 is given off, and a denser, heavier precipitate (the *heavy carbonate*) is formed, which varies in composition, according to the length of time during which the boiling is continued, and to the presence or absence of excess of sodium carbonate. The pharmaceutical product is a mixture of magnesium carbonate and magnesium hydroxide.

Analytical Characters.—(1) Ammonium hydroxide: voluminous, white ppt. from neutral solutions. (2) Potash or soda: voluminous white ppt. from warm solutions, prevented by the presence of NH_4 salts, and of certain organic substances. (3) Ammonium carbonate: slight ppt. from hot solutions; prevented by the presence of NH_4 salts. (4) Sodium or potassium carbonate: white ppt., best from hot solution; prevented by the presence of NH_4 compounds. (5) Disodic phosphate: white ppt. in hot, not too dilute solutions. (6) Oxalic acid: nothing alone, but in presence of NH_4OH , a white ppt.; not formed in presence of salts of NH_4 .

ZINC.

Symbol=Zn—*Atomic weight*=65—(*International* = 65.37)—*Molecular weight*=65—*Sp. gr.*=6.862–7.215.

Occurs principally in *calamine* (ZnCO_3); and *blende* (ZnS); also as oxide and silicate; never free. It is separated from its ores by calcining, roasting, and distillation.

It is a bluish-white metal; crystalline, granular, or fibrous; quite malleable and ductile when pure. The commercial metal is usually brittle. At 130° – 150° it is pliable, and becomes brittle again above 200° – 210° .

At 500° it burns in air, with a greenish-white flame, and gives off snowy-white flakes of the oxide. In moist air it becomes coated with a film of zinc oxide and carbonate. It decomposes steam when heated.

Pure H_2SO_4 and pure Zn do not react together in the cold. If the acid is diluted, however, it dissolves the Zn, with evolution of H , and formation of ZnSO_4 , in the presence of a trace of Pt or Cu. The commercial metal dissolves readily in dilute H_2SO_4 , with evolution of H , and formation of ZnSO_4 , the action being accelerated in presence of Pt, Cu, or As. Zinc surfaces, thoroughly coated with a layer of an amalgam of Hg and Zn, are only attacked by H_2SO_4 if they form part of closed galvanic circuit; hence the zincs of galvanic batteries are protected by *amalgamation*. Zinc also decomposes HNO_3 , HCl , and acetic acid. Zinc dissolves in strong solutions of the caustic alkalies with evolution of hydrogen and formation of double oxides (zincates): $\text{Zn} + 2\text{KOH} = \text{Zn}_2\text{K}_2 + \text{H}_2$. It also decomposes many metallic salts in solution with deposition of the metal.

When required for toxicological analysis, zinc must be perfectly free from As, and sometimes from P. It is better to test samples until a pure one is found, than to attempt the purification of a contaminated metal.

Zinc surfaces are readily attacked by weak organic acids. Vessels of *galvanized iron* or *sheet zinc* should therefore never be used to contain articles of food or medicines.

Zinc Oxide—*Zinci oxidum* (U. S. P.)— ZnO —81—is prepared either by calcining the precipitated carbonate, or by burning Zn in a current of air. An impure oxide, known as **tutty**, is deposited in the flues of zinc furnaces, and in those in which brass is fused. When obtained by calcination of the carbonate, it forms a soft, white, tasteless, and odorless powder. When produced by burning the metal, it occurs in light, voluminous, white masses. It is neither fusible, volatile, nor decomposable by heat, and is completely insoluble in neutral solvents. It dissolves in dilute acids, with formation of the corresponding salts.

It is used in the arts as a white pigment in place of lead carbonate, and is not darkened by H_2S .

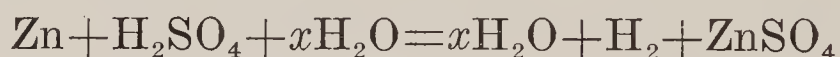
Zinc Hydroxide— $\text{Zn}(\text{OH})_2$ —99—is not formed by union of ZnO and H_2O ; but is produced when a solution of a Zn salt is treated with KOH . Freshly prepared, it is very soluble in alkalies, and in solutions of NH_4 salts.

Zinc Chloride—*Butter of zinc*—*Zinci chloridum* (U. S. P.)— $\text{ZnCl}_2 + \text{Aq}$ —136+18—is obtained by dissolving Zn in HCl , or by heating Zn in Cl . It is a soft, white, very deliquescent, fusible, volatile mass; very soluble in H_2O , somewhat less so in alcohol. Its solution has a burning, metallic taste; destroys vegetable tissues; dissolves silk; and exerts a strong dehydrating action upon organic substances in general.

In dilute solution it is used as a disinfectant and antiseptic (*Burnett's fluid*), as a preservative of wood and as an embalming injection.

Liquor zinci chloridi (U. S. P.) is an aqueous solution of zinc chloride containing not less than 48.5 per cent. nor more than 52 per cent. of ZnCl_2 .

Zinc Sulphate—*White vitriol*—*Zinci sulphas* (U. S. P.)— $\text{ZnSO}_4 + 7\text{Aq}$ —161+126—is formed when Zn, ZnO , ZnS , or ZnCO_3 is dissolved in diluted H_2SO_4 :



It crystallizes below 30° with 7 Aq; at 30° with 6 Aq; between 40° – 50° with 5 Aq; at 0° from concentrated acid solution with 4 Aq. From a boiling solution it is precipitated by concentrated H_2SO_4 with 2 Aq; from a saturated solution at 100° with 1 Aq; and anhydrous, when the salt with 1 Aq is heated to 238° .

The salt usually met with is that with 7 Aq, which is in large, colorless, four-sided prisms; efflorescent; very soluble in H_2O , sparingly soluble in weak alcohol. Its solutions have a strong, styptic taste: coagulate albumen when added in moderate quantity, the coagulum dissolving in an excess; and form insoluble precipitates with the tannins.

Carbonates.—**Zinc Carbonate**— ZnCO_3 —125—occurs in nature as *calamine*. If an alkaline carbonate is added to a solution of a Zn

salt, the neutral carbonate, as in the case of Mg, is not formed, but an oxycarbonate, $n\text{ZnCO}_3$, $n\text{Zn}(\text{OH})_2$, whose composition varies with the conditions under which it is formed.

Analytical Characters.—(1) K, Na or NH_4 hydroxide: white ppt., soluble in excess. (2) Carbonate of K or Na: white ppt., in absence of NH_4 salts. (3) Hydrogen sulphide, in neutral solution: white ppt. In presence of an excess of a mineral acid, the formation of this ppt. is prevented, unless sodium acetate is also present. (4) Ammonium sulphhydrate: white ppt., insoluble in excess, in KOH, NH_4OH , or acetic acid; soluble in dilute mineral acids. (5) Ammonium carbonate: white ppt., soluble in excess. (6) Disodic phosphate, in absence of NH_4 salts: white ppt., soluble in acids or alkalies. (7) Potassium ferrocyanide: white ppt., insoluble in HCl.

Action on the Economy—All the compounds of Zn which are soluble in the digestive fluids behave as true poisons; and solutions of the chloride (in common use by tinsmiths, and in disinfecting fluids) has also well-marked corrosive properties. When Zn compounds are taken, it is almost invariably by mistake for other substances: the sulphate for Epsom salt, and solutions of the chloride for various liquids, such as gin, fluid magnesia, vinegar, etc.

Metallic zinc is dissolved by solutions containing NaCl, or organic acids, for which reason articles of food kept in vessels of galvanized iron become contaminated with zinc compounds, and, if eaten, produce more or less intense symptoms of intoxication. For the same reason materials intended for analysis in cases of supposed poisoning, *should never be packed in jars closed by zinc caps.*

CADMIUM.

Symbol=Cd—*Atomic weight*=112—(*International*=112.40)—*Molecular weight*=112—*Sp. gr.*=8.604.

A white metal, malleable and ductile at low temperature, brittle when heated; which accompanies Zn in certain of its ores. It resembles zinc in its physical as well as its chemical characters. It is used in certain fusible alloys, and its iodide is used in photography.

Analytical Characters.—Hydrogen sulphide: bright yellow ppt.; insoluble in NH_4HS , and in dilute acids and alkalies, soluble in boiling HNO_3 or HCl.

V. ALUMINIUM GROUP.

GLUCINUM—ALUMINIUM—SCANDIUM—GALLIUM—INDIUM.

The existence of the aluminates, such as $\text{K}_2\text{Al}_2\text{O}_4$, would seem to place aluminium in the amphoteric class. These compounds, which are formed by the reactions: $\text{Al}(\text{OH})_3 + \text{KOH} = \text{KAlO}_2 + 2\text{H}_2\text{O}$, and $\text{Al}_2 + 2\text{KOH} + 2\text{H}_2\text{O} = 2\text{KAlO}_2 + 3\text{H}_2$, are double oxides rather than salts. They resemble the zincates and what has been said concerning those compounds (see p. 175) applies also to the aluminates.

ALUMINIUM.

Symbol=Al—*Atomic weight*=27—(*International*=27.1)—*Molecular weight*=54—*Sp. gr.*=2.56–2.67.

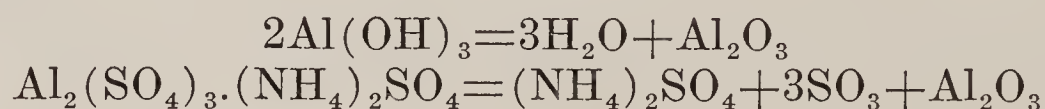
Occurrence.—Never found in the free state, but abundant in the clays as *silicate*. Also in *feldspar*, *mica*, and *garnet*, *topaz*, and *emerald*. As a fluoride in *cryolite*, and as a hydroxide in *bauxite*.

Preparation.—(1) By decomposing vapor of aluminium chloride by Na or K (Wöhler). (2) Aluminium hydroxide, mixed with sodium chloride and charcoal, is heated in Cl, by which a double chloride of Na and Al (NaAlCl_4) is formed. This is then heated with Na, when Al and NaCl are produced. (3) These “chemical methods” have been replaced, in the industrial preparation of aluminium, by the electrolytic method, in which a mixture of cryolite and bauxite is treated in an electric furnace.

Properties.—*Physical.*—A bluish-white metal; hard; quite malleable, and ductile, when annealed from time to time; slightly magnetic; a good conductor of electricity; non-volatile; very light, and exceedingly sonorous.

Chemical.—It is not affected by air or O, except at very high temperatures, and then only superficially. If, however, it contains Si, it burns readily in air, forming aluminium silicate. It does not decompose H_2O at a red heat; but in contact with Cu, Pt, or I, it does so at 100° . It combines directly with B, Si, Cl, Br, and I. It is attacked by HCl, gaseous or in solution, with evolution of H, and formation of AlCl_3 . It dissolves in alkaline solutions, with formation of **aluminates**, and liberation of H. It alloys with Cu to form a golden yellow metal (**aluminium bronze**).

Aluminium Oxide—*Alumina*— Al_2O_3 —102—occurs in nature, nearly pure, as *corundum*, *emery*, *ruby*, *sapphire*, and *topaz*; and is formed artificially, by calcining the hydrate, or ammonium alum, at a red heat:



It is a light, white, odorless, tasteless powder; fuses with difficulty; and, on cooling, solidifies in very hard crystals. Unless it has been heated to bright redness, it combines with H_2O , with elevation of temperature. It is almost insoluble in acids and alkalies. H_2SO_4 , diluted with an equal bulk of H_2O , dissolves it slowly as $(\text{Al}_2)(\text{SO}_4)_3$. Fused potash and soda combine with it to form aluminates. It is not reduced by charcoal.

Aluminium Hydroxide—*Aluminium hydrate*—**Alumini hydroxidum**—(U. S. P.)— $\text{Al}(\text{OH})_3$ —78—is formed when a solution of alu-

minium salt is decomposed by an alkali, or alkaline carbonate. It constitutes a gelatinous mass, which, when dried, leaves an amorphous, translucent mass; and, when pulverized, a white, tasteless, amorphous powder. When the liquid in which it is formed contains coloring matters, these are carried down with it, and the dried deposits are used as pigments, called **lakes**. It is used as a mordant.

When freshly precipitated, it is insoluble in H_2O ; soluble in acids, and in solutions of the fixed alkalies. When dried at a temperature above 50° , or after 24 hours' contact with the mother liquor, its solubility is greatly diminished. With acids it forms salts of aluminium; and with alkalies, aluminates of the alkaline metal. Heated to near redness, it is decomposed into Al_2O_3 , and H_2O . A soluble modification is obtained by dialyzing a solution of $Al(OH)_3$ in $AlCl_3$, or by heating a dilute solution of aluminium acetate for 24 hours.

Aluminium Chloride— $AlCl_3$ —133.5—is prepared by passing Cl over a mixture of Al_2O_3 and C , heated to redness, or by heating clay in a mixture of gaseous HCl and vapor of CS_2 .

It crystallizes in colorless, hexagonal prisms; fusible; volatile; deliquescent; very soluble in H_2O and in alcohol. From a hot, concentrated solution, it separates in prisms with 12Aq.

The disinfectant called **chloralum** is a solution of impure $AlCl_3$.

Aluminium Sulphate— $Al_2(SO_4)_3 + 18Aq$ —342+324—is obtained by dissolving $Al(OH)_3$ in H_2SO_4 or (industrially) by heating clay with H_2SO_4 .

It crystallizes, with difficulty, in thin, flexible plates; soluble in H_2O ; very sparingly soluble in alcohol. Heated, it fuses in its Aq, which it gradually loses up to 200° , when a white, amorphous powder, $Al_2(SO_4)_3$, remains: this is decomposed at a red heat, leaving a residue of pure alumina.

Alums—are double sulphates of an univalent, alkaline, metal, and trivalent metal (Fe , Mn , Cr , or Al). When crystallized, they have the general formula: $M^iM^{iii}(SO_4)_2 + 12Aq$. They are isomorphous with each other.

Alum—Alumen (U. S. P.)—The official alum is the *ammonium alum* (ammonium aluminium sulphate) $NH_4.Al(SO_4)_2 + 12Aq$ —237+216, or the *potassium alum* (potassium aluminium sulphate) $K.Al(SO_4)_2 + 12Aq$ —258+216.

It is formed when solutions of the sulphates are mixed in suitable proportions. It crystallizes in large, transparent, regular octahedra; has a sweetish, astringent taste, and is readily soluble in H_2O .

Dried alum, burnt alum=alumen exsiccatum (U. S. P.) is anhydrous— $Al.NH_4.(SO_4)_2$ or $Al.K(SO_4)_2$; and is alum from which the water of crystallization has been driven out by heat. It is a white powder, readily soluble in boiling water, but slowly soluble in cold

water. Alum is used in dyeing, and in purification of water by precipitation.

Silicates—are very abundant in the different varieties of *clay*, *feldspar*, *albite*, *labradorite*, *mica*, etc. The *clays* are hydrated aluminium silicates, more or less contaminated with alkaline and earthy salts and iron, to which last certain clays owe their color. The purest is **kaolin**, or porcelain clay, a white or grayish powder. They are largely used in the manufacture of the different varieties of bricks, terra cotta, pottery, and porcelain. *Porcelain* is made from the purer clays, mixed with sand and feldspar; the former to prevent shrinkage, the latter to bring the mixture into partial fusion, and to render the product translucent. The fashioned articles are subjected to a first baking. The porous, baked clay is then coated with a *glaze*, usually composed of oxide of lead, sand, and salt. During a second baking the glaze fuses, and coats the article with a hard, impermeable layer. The coarser articles of pottery are glazed by throwing sodium chloride into the fire; the salt is volatilized, and on contact with the hot aluminium silicate, deposits a coating of the fusible sodium silicate, which hardens on cooling.

Analytical Characters.—(1) Potash, or soda: white ppt., soluble in excess. (2) Ammonium hydroxide: white ppt., almost insoluble in excess, especially in presence of ammoniacal salts. (3) Sodium phosphate: white ppt., readily soluble in KOH and NaOH, but not in NH_4OH ; soluble in mineral acids, but not in acetic acid. (4) Blow-pipe—on charcoal does not fuse, and moistened with cobalt nitrate solution turns dark sky-blue.

VI. NICKEL GROUP.

NICKEL—COBALT.

These two elements bear some resemblance chemically to those of the Fe group; from which they differ in forming, so far as known, no compounds similar to the ferrates, chromates, and manganates. They are often associated with iron, and, like iron, are attracted by the magnet.

NICKEL.

Symbol=Ni—*Atomic weight*=58—(*International*=58.68)—*Sp. gr.*=8.637.

Occurs in combination with S, and with S and As.

It is a white metal, hard, slightly magnetic, not tarnished in air. *German silver* is an alloy of Ni, Cu, and Zn. Nickel is now extensively used for plating upon other metals, and for the manufacture of dishes, etc., for use in the laboratory. Its salts are green.

Nickelous Sulphate— NiSO_4 —is obtained by dissolving the metal, hydroxide or carbonate in H_2SO_4 . It forms green crystals with 7 Aq,

and combines with $(\text{NH}_4)_2\text{SO}_4$ to form a double sulphate, used in the nickel-plating bath, for which use it must be free from K or Na.

Analytical Characters.—(1) Ammonium sulphhydrate: black ppt.; insoluble in excess. (2) Potash or soda: apple-green ppt., in absence of tartaric acid; insoluble in excess. (3) Ammonium hydrate: apple-green ppt.; soluble in excess; forming a violet solution, which deposits the apple-green hydrate, when heated with KOH.

COBALT.

Symbol=Co—*Atomic weight*=59—(*International*=58.97)—*Sp. gr.*=8.5–8.7.

Occurs in combination with As and S. Its salts are red when hydrated, and usually blue when anhydrous. Its phosphate is used as a blue pigment.

Analytical Characters.—(1) Ammonium sulphhydrate: black ppt.; insoluble in excess. (2) Potash: blue ppt.; turns red, slowly in the cold, quickly when heated; not formed in the cold in the presence of NH_4 salts. (3) Ammonium hydroxide: blue ppt.; turns red in absence of air, green in its presence.

VII. COPPER GROUP.

COPPER—MERCURY.

Each of these elements forms two series of compounds. One is univalent, Cu' or Hg' , and is distinguished by the termination **ous**; the other is bivalent, Cu'' or Hg'' , and is designated by the termination **ic**. Some writers double the formulæ of the **ous** salts, but the more modern practice is to write HgCl and not Hg_2Cl_2 , etc.

COPPER.

Symbol=Cu (*Cuprum*)—*Atomic weight*=63—(*International*=63.57)—*Molecular weight*=127—*Sp. gr.*=8.914–8.952.

Occurrence.—It is found free, in crystals or amorphous masses, sometimes of great size; also as sulphide, *copper pyrites*; oxide, *ruby ore* and *black oxide*; and basic carbonate, *malachite*, a mixed carbonate and hydroxide of copper, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

Properties.—*Physical.*—A yellowish-red metal; dark-brown when finely divided; very malleable, ductile, and tenacious; a good conductor of heat and electricity; has a peculiar, metallic taste, and a characteristic odor.

Chemical.—It is unaltered in dry air at the ordinary temperature; but, when heated to redness, is oxidized to CuO . In damp air it

becomes coated with a brownish film of oxide; a green film of basic carbonate; or, in salt air, a green film of basic chloride. Hot H_2SO_4 dissolves it with formation of CuSO_4 and SO_2 . It is dissolved by HNO_3 with formation of $\text{Cu}(\text{NO}_3)_2$ and NO ; and by HCl with liberation of H . Weak acids form with it soluble salts, in presence of air and moisture. It is dissolved by NH_4OH , in presence of air, with formation of a blue solution. It combines directly with Cl , frequently with light.

Oxides.—**Cuprous Oxide**—*red oxide of copper*— Cu_2O —143—is formed by calcining a mixture of CuCl and Na_2CO_3 ; or a mixture of CuO and Cu . It is a red or yellow powder; permanent in air; sp. gr. 5.749–6.093; fuses at a red heat; easily reduced by C or H . Heated in air it is converted into CuO .

Cupric Oxide—*Black oxide of copper*— CuO —79—is prepared by heating Cu to dull redness in air; or by calcining $\text{Cu}(\text{NO}_3)_2$; or by prolonged boiling of the liquid over a precipitate, produced by heating a solution of a cupric salt, in presence of glucose, with KOH . By the last method it is sometimes produced in Trommer's test for glucose, when an excessive quantity of CuSO_4 has been used.

It is a black, or dark reddish-brown, amorphous solid; readily reduced by C , H , Na , or K at comparatively low temperatures. When heated with organic substances, it gives up its O , converting the C into CO_2 , and the H into H_2O :



a property which renders it valuable in organic analysis, as by heating a known weight of organic substances with CuO , and weighing the amount of CO_2 and H_2O produced, the percentage of C and H may be obtained. It dissolves in acids with formation of salts.

Hydroxides—**Cuprous Hydroxide**— CuOH —80—is formed as a yellow or red powder when mixed solutions of CuSO_4 and KOH are heated in presence of glucose. By boiling the solution it is rapidly dehydrated with formation of Cu_2O .

Cupric Hydroxide— $\text{Cu}(\text{OH})_2$ —97—is formed by the action of KOH upon solution of CuSO_4 , in absence of reducing agents and in the cold. It is a bluish, amorphous powder; very unstable, and readily dehydrated, with formation of CuO .

Chlorides.—**Cuprous Chloride**— CuCl —98.5—is prepared by heating Cu with one of the chlorides of Hg ; by dissolving Cu_2O in HCl , without contact of air; or by the action of reducing agents on solutions of CuCl_2 . It is a heavy, white powder; turns violet and blue by exposure to light; soluble in HCl ; insoluble in H_2O . It forms a crystallizable compound with CO ; and its solution in HCl is used in analysis to absorb that gas.

Cupric Chloride— CuCl_2 —134—is formed by dissolving Cu in aqua regia. If the Cu is in excess, it reduces CuCl_2 to CuCl . It crystallizes in bluish-green, rhombic prisms with 2 Aq ; deliquescent; very soluble in H_2O and in alcohol.

Cupric Nitrate— $\text{Cu}(\text{NO}_3)_2$ —187—is formed by dissolving Cu , CuO , or

CuCO_3 in HNO_3 . It crystallizes at 20° – 25° with 3 Aq; below 20° with 6 Aq, forming blue, deliquescent needles. Strongly heated, it is converted into CuO .

Cupric Sulphate—Blue vitriol—Bluestone—Cupri sulphas (U. S. P.)— $\text{CuSO}_4 + 5\text{Aq}$ —159+90—is prepared: (1) by roasting CuS ; (2) from the water of copper mines; (3) by exposing Cu , moistened with dilute H_2SO_4 , to air; (4) by heating Cu with H_2SO_4 .

As ordinarily crystallized, it is in fine, blue, oblique prisms; soluble in H_2O ; insoluble in alcohol; efflorescent in dry air at 15° , losing 2 Aq. At 100° it still retains 1 Aq, which it loses at 230° , leaving a white, amorphous powder of the anhydrous salt, which, on taking up H_2O , resumes its blue color. Its solutions are blue, acid, styptic, and metallic in taste.

When NH_4OH is added to a solution of CuSO_4 , a bluish-white precipitate falls, which redissolves in excess of the alkali, to form a deep blue solution. Strong alcohol floated over the surface of this solution separates long, right rhombic prisms, having the composition $\text{CuSO}_4 \cdot 4\text{NH}_3 + \text{H}_2\text{O}$, which are very soluble in H_2O . This solution constitutes **ammonio-sulphate of copper** or **aqua sapphirina**.

Cupric Arsenite—Scheele's green—Mineral green—is a mixture of cupric arsenite, HCuAsO_3 , and hydroxide; prepared by adding potassium arsenite to solution of CuSO_4 . It is a grass-green powder, insoluble in H_2O ; soluble in NH_4OH , or in acids. Exceedingly poisonous.

Schweinfurt Green—Mitis green or Paris green—is the most frequently used, and the most dangerous of the cupro-arsenical pigments. It is prepared by adding a thin paste of neutral cupric acetate with H_2O to a boiling solution of arsenous acid, and continuing the boiling during a further addition of acetic acid. It is an insoluble, green, crystalline powder, having the composition $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu} + 3\text{Cu}(\text{AsO}_2)_2$, and is therefore cupric aceto-metarsenite. It is decomposed by prolonged boiling in H_2O , by aqueous solutions of the alkalies, and by the mineral acids.

Acetates.—Cupric Acetate— $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Aq}$ —181+18—is formed when CuO or verdigris is dissolved in acetic acid; or by decomposition of a solution of CuSO_4 by $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. It crystallizes in large, bluish-green prisms, which lose their Aq at 140° . At 240° – 260° they are decomposed with liberation of glacial acetic acid.

Basic Acetates.—Verdigris—is a substance prepared by exposing to air piles composed of alternate layers of grape-skins and plates of copper, and removing the bluish-green coating from the copper. It is a mixture, in varying proportions, of three different substances: $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu}(\text{OH}) + 5\text{Aq}$; $[(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu}]_2$, $\text{Cu}(\text{OH})_2 + 5\text{Aq}$; and $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu}, 2(\text{CuH}_2\text{O}_2)$.

Analytical Characters.—CUPROUS—are very unstable and readily converted into cupric compounds. (1) Potash: white ppt.; turning brownish. (2) Ammonium hydroxide, in absence of air: a colorless liquid; turns blue in air.

CUPRIC—are white when anhydrous; when soluble in H_2O they form blue or green, acid solutions. (1) Hydrogen sulphide: black ppt.; insoluble in KHS or NaHS ; sparingly soluble in NH_4HS ; soluble in hot concentrated HNO_3 and in KCN . (2) Alkaline sulphhydrates: same as H_2S . (3) Potash, or soda: pale blue ppt.; insoluble

in excess. If the solution be heated over the ppt., the latter contracts and turns black. (4) Ammonium hydroxide, in small quantity: pale blue ppt.; in larger quantity: deep blue solution. (5) Potassium or sodium carbonate: greenish-blue ppt.; insoluble in excess; turning black when the liquid is boiled. (6) Ammonium carbonate: pale blue ppt.; soluble with deep-blue color in excess. (7) Potassium cyanide: greenish-yellow ppt.; soluble in excess. (8) Potassium ferrocyanide: chestnut-brown ppt.; insoluble in weak acids; decolorized by KOH. (9) Iron is coated with metallic Cu.

Action on the Economy.—Certain of the copper compounds, such as the sulphate, having a tendency to combine with protein and other animal substances, produce symptoms of irritation by their direct local action, when brought in contact with the gastric or intestinal mucous membrane. A characteristic symptom of such irritation is the vomiting of a greenish matter, which develops a blue color upon the addition of NH_4OH .

Severe illness, and even death, has followed the use of food which has been in contact with imperfectly tinned copper vessels. It is probable that the poisonous action attributed to copper is sometimes due to other substances. The tin and solder used in the manufacture of copper utensils contain lead, and in some cases of so-called copper-poisoning, the symptoms have been such as are as consistent with lead-poisoning as with copper-poisoning. Copper is also notoriously liable to contamination with arsenic, and it is by no means improbable that compounds of that element are the active poisonous agents in some cases of supposed copper-intoxication. Nor is it improbable that articles of food allowed to remain exposed to air in copper vessels should undergo those peculiar changes which result in the formation of poisonous substances, such as the sausage- or cheese-poisons, or the ptomaines.

The *treatment*, when irritant copper compounds have been taken, should consist in the administration of white of egg or of milk, with whose proteins an inert compound is formed by the copper salt. If vomiting does not occur spontaneously, it should be induced by the usual methods.

The detection of copper in the viscera after death is not without interest, especially if arsenic has been found, in which case its discovery or non-discovery enables us to differentiate between poisoning by the arsenical greens, and that by other arsenical compounds. The detection of mere traces of copper is of no significance, because, although copper is not a physiological constituent of the body, it is almost invariably present, having been taken with the food.

Pickles and canned vegetables are sometimes intentionally *greened* by the addition of copper; this fraud is readily detected by inserting a large needle into the pickle or other vegetable; if copper is present the steel will be found to be coated with copper after half an hour's contact.

MERCURY.

Symbol=Hg (*Hydrargyrum*)—*Atomic weight*=200—(*International*=200.6)—*Molecular weight*=200—*Sp. gr. of liquid*=13.596; *of vapor*=6.97.

Occurrence.—Chiefly as *cinnabar* (HgS); also in small quantity free and as chloride.

Preparation.—The commercial product is usually obtained by

simple distillation in a current of air: $\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$. If required pure, it must be freed from other metals by distillation, and agitation of the redistilled product with mercurous nitrate solution, solution of FeCl_3 , or dilute HNO_3 .

Properties.—*Physical.*—A bright metallic liquid, commonly known as *quicksilver*; volatile at all temperatures. Crystallizes in octahedra of sp. gr. 14.0. When pure, it rolls over a smooth surface in round drops. The formation of tear-shaped drops indicates the presence of impurities.

Chemical.—If pure, it is not altered by air at the ordinary temperature, but, if contaminated with foreign metals, its surface becomes dimmed. Heated in air, it is oxidized superficially to HgO . It does not decompose H_2O . It combines directly with Cl , Br , I , and S . It alloys readily with most metals to form **amalgams**. It amalgamates with Fe and Pt with difficulty. Hot, concentrated, H_2SO_4 dissolves it, with evolution of SO_2 , and formation of HgSO_4 . It dissolves in cold HNO_3 , with formation of a nitrate.

An alloy is a substance composed of two or more metals.

An amalgam is an alloy containing mercury.

Elementary mercury is insoluble in H_2O , and probably in the digestive liquids. It enters, however, into the formation of three medicinal agents: **hydrargyrum cum creta** (U. S. P.), containing 38 per cent. of Hg ; **massa hydrargyri** (U. S. P.), containing 33 per cent. of Hg ; and **unguentum hydrargyri** (U. S. P.), all of which owe their efficacy, not to the metal itself, but to a certain proportion of oxide, produced during their manufacture. The fact that blue mass is more active than mercury with chalk is due to the greater proportion of oxide contained in the former. It is also probable that absorption of vapor of Hg by cutaneous surfaces is attended by its conversion into HgCl_2 .

Oxides.—**Mercurous Oxide**—*Black oxide of mercury*— Hg_2O —416—is obtained by adding a solution of HgNO_3 to an excess of solution of KOH . It is a brownish black, tasteless powder; very prone to decomposition into HgO and Hg . It is converted into HgCl by HCl ; and by other acids into the corresponding mercurous salts.

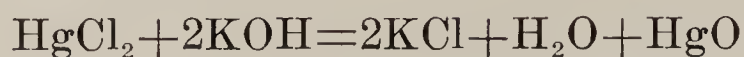
It exists in **black wash**, obtained by mixing together calomel and lime water:



Mercuric Oxide—*Yellow oxide of mercury*—*Red oxide of mercury*—**Hydrargyri oxidum flavum** (U. S. P.)—**Hydrargyri oxidum rubrum** (U. S. P.)— HgO —216—is prepared by two methods: (1) by calcining $\text{Hg}(\text{NO}_3)_2$, as long as brown fumes are given off (*Hydr. oxid. rubr.*):

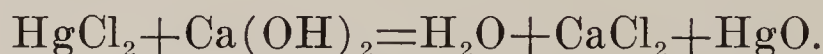


or, (2) by precipitating a solution of a mercuric salt by excess of KOH (*Hydr. oxid. flavum*):



The products obtained, although the same in composition, differ in physical characters and in the activity of their chemical actions. That obtained by (1) is red and crystalline; that obtained by (2) is yellow and amorphous. The latter is much the more active in its chemical and medicinal actions.

It is very sparingly soluble in H_2O , the solution having an alkaline reaction, and a metallic taste. It exists both in solution and in suspension in **yellow wash**, prepared by the action of $\text{Ca}(\text{OH})_2$ on mercuric chloride:



Exposed to light and air, it turns black, more rapidly in presence of organic matter, giving off O, and liberating Hg: $\text{HgO} = \text{Hg} + \text{O}$. It decomposes the chlorides of many metallic elements in solution, with formation of a metallic oxide and mercuric oxychloride.

Chlorides.—Mercurous Chloride—Protochloride or mild chloride of mercury—Calomel—Hydrargyri chloridum mite (U. S. P.)— HgCl —235.5—is obtained by heating a mixture of mercuric sulphate, mercury, and sodium chloride, when the calomel (which volatilizes) is condensed:



Calomel is also formed in a number of other reactions: (1) By the action of Cl upon excess of Hg. (2) By the action of Hg upon FeCl_3 . (3) By the action of HCl, or of a chloride, upon Hg_2O , or upon a mercurous salt. (2) By the action of reducing agents, including Hg, upon HgCl_2 .

Calomel crystallizes in nature, and, when sublimed, in quadratic prisms. When precipitated it is deposited as a heavy, amorphous, white powder, faintly yellowish, and producing a yellowish mark when rubbed upon a dark surface. It sublimes, without fusing, between 420° and 500° , is insoluble in cold H_2O and in alcohol; soluble in boiling H_2O to the extent of 1 part in 12,000. When boiled with H_2O for some time, it suffers partial decomposition, Hg is deposited and HgCl_2 dissolves.

Although HgCl is insoluble in H_2O , in dilute HCl and in pepsin solution, it is dissolved at the body temperature in an aqueous solution of pepsin acidulated with HCl.

When exposed to light, calomel becomes yellow, then gray, owing to partial decomposition, with liberation of Hg and formation of HgCl_2 : $2\text{HgCl} = \text{Hg} + \text{HgCl}_2$. It is converted into HgCl_2 by Cl or aqua regia: $2\text{HgCl} + \text{Cl}_2 = 2\text{HgCl}_2$. In the presence of H_2O , I converts it into a mixture of HgCl_2 and HgI_2 : $2\text{HgCl} + \text{I}_2 = \text{HgCl}_2 +$

HgI_2 . It is also converted into HgCl_2 by HCl and by alkaline chlorides: $2\text{HgCl}=\text{HgCl}_2+\text{Hg}$. This change occurs in the stomach when calomel is taken internally, and that to such an extent when large quantities of NaCl are taken with the food, that calomel cannot be used in naval practice as it may be with patients who do not subsist upon salt provisions. It is converted by KI into HgI : $\text{HgCl}+\text{KI}=\text{KCl}+\text{HgI}$; which is then decomposed by excess of KI into Hg and HgI_2 , the latter dissolving: $2\text{HgI}=\text{Hg}+\text{HgI}_2$. Solutions of the sulphates of Na , K and NH_4 dissolve notable quantities of HgCl . The hydroxides and carbonates of K and Na decompose it with formation of H_2O : $2\text{HgCl}+\text{Na}_2\text{CO}_3=\text{Hg}_2\text{O}+\text{CO}_2+2\text{NaCl}$; and the Hg_2O so formed is decomposed into HgO and Hg . If alkaline chlorides are present, they react upon the HgO so produced with formation of HgCl_2 .

Mercuric Chloride—*Perchloride or bichloride of mercury*—**Corrosive sublimate**—*Hydrargyri chloridum corrosivum* (U. S. P); — HgCl_2 —271—is prepared by heating a mixture of 5 pts. dry HgSO_4 with 5 pts. dry NaCl , and 1 pt. MnO_2 in a glass vessel communicating with a condensing chamber.

It crystallizes by sublimation in octahedra, and by evaporation of its solutions in flattened, right rhombic prisms; fuses at 265° , and boils at about 295° ; soluble in H_2O and in alcohol; very soluble in hot HCl , the solution gelatinizing on cooling. Its solutions have a disagreeable, acid, styptic taste, and are highly poisonous. Although HgCl_2 is heavier than water (sp. gr.=5.4) when the crystalline powder is thrown upon water a portion floats for some time.

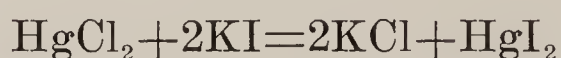
It is easily reduced to HgCl and Hg , and its aqueous solutions are so decomposed when exposed to light; a change which is retarded by the presence of NaCl . Heated with Hg , it is converted into HgCl . When dry HgCl_2 , or its solution, is heated with Zn , Cd , Ni , Fe , Pb , Cu , or Bi , those elements remove part or all of its Cl , with separation of HgCl or Hg . Its solution is decomposed by H_2S , with separation of a yellow sulphochloride, which, with an excess of the gas, is converted into black HgS . It is soluble without decomposition in H_2SO_4 , HNO_3 , and HCl . It is decomposed by KOH or NaOH , with separation of a brown oxychloride if the alkaline hydroxide is in limited quantity; or of the orange-colored HgO if it is in excess. A similar decomposition is effected by $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$; which does not, however, take place in presence of an alkaline chloride, or of certain organic matters, such as sugar and gum. Many organic substances decompose it into HgCl or Hg , especially under the influence of sunlight. Thus in sunlight it is reduced by oxalic acid, which is itself oxidized to carbon dioxide: $2\text{HgCl}_2+\text{C}_2\text{O}_4\text{H}_2=2\text{HgCl}+2\text{CO}_2+2\text{HCl}$. For this reason it behaves as an oxidant: $2\text{HgCl}_2+\text{H}_2\text{O}=2\text{HgCl}+2\text{HCl}+\text{O}$. Albumin forms with it a white precipitate, which is insoluble in H_2O , but soluble in

an excess of fluid albumin and in solutions of alkaline chlorides. It is a very energetic germicide.

Mercurammonium Chloride—*White precipitate*—*Ammoniated mercury*—**Hydrargyrum ammoniatum** (U. S. P.)— NH_2HgCl —251.5—is prepared by adding a slight excess of NH_4OH to a solution of HgCl_2 . It contains 79 per cent. of Hg; and is a white powder, insoluble in alcohol, ether, and cold H_2O : decomposed by hot H_2O , with separation of a heavy, yellow powder. It is entirely volatile, without fusion. The *fusible white precipitate* is formed in small crystals when a solution containing equal parts of HgCl_2 and NH_4Cl is decomposed by Na_2CO_3 . It is **mercurdiammonium chloride**, $\text{NH}_2\text{Hg}, \text{NH}_4\text{Cl}_2$.

Iodides.—**Mercurous Iodide**—*Protoiodide* or *yellow iodide*—**Hydrargyri iodidum flavum** (U. S. P.)— HgI —327—is prepared by grinding together 200 pts. Hg and 127 pts. I with a little alcohol, until a green paste is formed. It is a greenish-yellow, amorphous powder, insoluble in H_2O and in alcohol. When heated, it turns brown, and volatilizes completely. When exposed to light, or even after a time in the dark, it is decomposed into HgI_2 and Hg. The same decomposition is brought about instantly by KI; more slowly by solutions of alkaline chlorides, and by HCl when heated. NH_4OH dissolves it with separation of a gray precipitate.

Mercuric Iodide—*Biniodide* or *red iodide*—**Hydrargyri iodidum rubrum** (U. S. P.)— HgI_2 —454—is obtained by double decomposition between HgCl_2 and KI, care being had to avoid too great an excess of the alkaline iodide, that the soluble potassium iodhydrargyrate may not be formed:



It is sparingly soluble in H_2O ; but forms colorless solutions with alcohol. It dissolves readily in many dilute acids, and in solutions of ammoniacal salts, alkaline chlorides, and mercuric salts; and in solutions of alkaline iodides. Iron and copper convert it into HgI , then into Hg. The hydroxides of K and Na decompose it into oxide or oxyiodides, and combine with another portion to form iodhydrargyrate, which dissolve. NH_4OH separates from its solution a brown powder, and forms a yellow solution, which deposits white flocks.

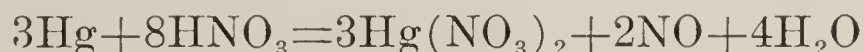
Mercuric Cyanide— $\text{Hg}(\text{CN})_2$ —252—is best prepared by heating together, for a quarter of an hour, potassium ferrocyanide, 1 pt.; HgSO_4 , 2 pts.; and H_2O , 8 pts. It crystallizes in quadrangular prisms; soluble in 8 pts. of H_2O , much less soluble in alcohol; highly poisonous. When heated dry it blackens, and is decomposed into $(\text{CN})_2$ and Hg; if heated in presence of H_2O it yields HCN, Hg, CO_2 , and NH_3 . Hot concentrated H_2SO_4 , and HCl, HBr, HI, and H_2S in the cold decompose it, with liberation of HCN. It is not decomposed by alkalies.

Nitrates — Mercurous Nitrate — $\text{HgNO}_3 + 2\text{Aq} - 262 + 36$ — is formed when excess of Hg is digested with moderately diluted HNO_3 :



It effloresces in air; fuses at 70° ; dissolves in a small quantity of hot H_2O , but with a larger quantity is decomposed with separation of the yellow, basic **trimercuric nitrate**, $\text{Hg}(\text{NO}_3)_2, 2\text{HgO} + \text{Aq}$.

Mercuric Nitrate— $\text{Hg}(\text{NO}_3)_2 - 324$ —is formed when Hg or HgO is dissolved in excess of HNO_3 , and the solution evaporated at a gentle heat:



This salt is soluble in H_2O , and exists in the volumetric standard solution used in *Liebig's process* for urea; and probably in *citrine ointment* = **Unguentum hydrarargyri nitratis** (U. S. P.).

Sulphates.—Mercurous Sulphate— $\text{Hg}_2\text{SO}_4 - 496$ —is a white, crystalline powder, formed by gently heating together 2 pts. Hg and 3 pts. H_2SO_4 , and causing the product to combine with 2 pts. Hg. Heated with NaCl it forms HgCl .

Mercuric Sulphate— $\text{HgSO}_4 - 296$ —is obtained by heating together Hg and H_2SO_4 , or Hg, H_2SO_4 , and HNO_3 . It is a white, crystalline, anhydrous powder, which, on contact with H_2O , is decomposed with formation of **trimercuric sulphate**, $\text{HgSO}_4, 2\text{HgO}$; a yellow, insoluble powder, known as **turpeth mineral**.

Analytical Characters.—MERCUROUS.—(1) Hydrochloric acid: white ppt.; insoluble in H_2O and in acids; turns black with NH_4OH ; when boiled with HCl, deposits Hg, while HgCl_2 dissolves. (2) Hydrogen sulphide; black ppt.; insoluble in alkaline sulphydrates, in dilute acids, and in KCN; partly soluble in boiling HNO_3 . (3) Potash: black ppt.; insoluble in excess. (4) Potassium iodide: greenish ppt.; converted by excess into Hg, which is deposited and HgI_2 , which dissolves.

MERCURIC.—(1) Hydrogen sulphide: black ppt. If the reagent is slowly added, the ppt. is first white, then orange, finally black. (2) Ammonium sulphydrate: black ppt.; insoluble in excess, except in the presence of organic matter. (3) Potash, or soda: yellow ppt.; insoluble in excess. (4) Ammonium hydroxide: white ppt.; soluble in great excess and in solutions of NH_4 salts. (5) Potassium carbonate: red ppt. (6) Potassium iodide: yellow ppt., rapidly turning to salmon color, then to red; easily soluble in excess of KI, or in great excess of mercuric salt. (7) Stannous chloride, in small quantity: white ppt.; in larger quantity: gray ppt.; and when boiled: deposit of globules of Hg.

Action on the Economy.—Metallic mercury is without action upon the animal economy. On contact, however, with alkaline chlorides it is converted into a soluble double chloride, and this the more readily the greater the degree

of subdivision of the metal. The mercurials insoluble in dilute HCl are also inert until they are converted into soluble compounds.

Mercuric chloride, a substance into which many other compounds of Hg are converted, when taken into the stomach or applied to the skin, not only has a distinctly corrosive action, by virtue of its tendency to unite with protein bodies, but, when absorbed, it produces well-marked poisonous effects, somewhat similar to those of arsenical poisoning. Indeed, owing to its corrosive action, and to its greater solubility and more rapid absorption, it is a more dangerous poison than As_2O_3 . In poisoning by HgCl_2 , the symptoms begin sooner after the ingestion of the poison than in arsenical poisoning, and those phenomena referable to the local action of the toxic are more intense. But the entire duration of the poisoning is greater. In fatal cases, death usually occurs in 5 to 12 days.

The *treatment* should consist in the administration of white of egg, not in too great quantity, and the removal of the compound formed, by emesis, before it has had time to redissolve in the alkaline chlorides contained in the stomach.

Absorbed Hg tends to remain in the system in combination with protein bodies, from which it may be set free, or, more properly, brought into soluble combination, at a period quite removed from the date of last administration, by the exhibition of alkaline iodides.

Mercury is *eliminated* principally by the saliva and urine, in which it may be readily detected. The fluid is faintly acidulated with HCl, and in it is immersed a short bar of Zn, around which a spiral of dentist's gold foil is wound in such a way as to expose alternate surfaces of Zn and Au. After 24 hours, if the saliva or urine contain Hg, the Au will be whitened by amalgamation; and, if dried and heated in the closed end of a small glass tube, will give off Hg, which condenses in globules, visible with the aid of a magnifier, in the cold part of the tube.

ORGANIC CHEMISTRY

COMPOUNDS OF CARBON.

In the beginning of the nineteenth century chemistry was divided into the two sections of **inorganic** and **organic**. The former treated of the products of the mineral world, the latter of **substances produced in organized bodies, vegetable or animal**. This subdivision, originally made upon the supposition that organic substances could only be produced by "vital processes," is retained only for convenience and because of the great number of the carbon compounds.

When it was found that organic substances were made up of a very few elements, and that they all contained carbon, Gmelin proposed to consider as organic substances **all such as contained more than one atom of C**, his object in thus limiting the minimum number of C atoms being that substances containing one atom of C, such as carbon dioxide and marsh gas, are formed in the mineral kingdom, and consequently, according to then existing views, could not be considered as *organic*. Such a distinction, still adhered to in some textbooks, of necessity leads to most incongruous results. Under it the first terms of the homologous series (see p. 193) of saturated hydrocarbons, CH_4 , alcohol, CH_4O , acids, CH_2O_2 , and all their derivatives are classed among *mineral* substances, while all the higher terms of the same series are *organic*. Under it urea, CON_2H_4 , the chief product of excretion of the animal body, is a *mineral* substance, but ethene, C_2H_4 , obtained from the distillation of coal, is *organic*.

The idea of organic chemistry conveyed by the definition: "**that branch of the science of chemistry which treats of the carbon compounds containing hydrogen**," is still more fantastic. Under it hydrocyanic acid, CNH , is *organic*, but the cyanides, CNK , are *mineral*. Oxalic acid, $\text{C}_2\text{O}_4\text{H}_2$, is *organic*, and potassium hydroxide, KOH , unquestionably *mineral*. If these two act upon each other in the proportion of 90 parts of the former to 56 of the latter, the *organic* monopotassic oxalate, $\text{C}_2\text{O}_4\text{HK}$, is formed, but if the proportion of KOH is doubled, other conditions remaining the same, the *mineral* dipotassic oxalate, $\text{C}_2\text{O}_4\text{K}_2$, is produced. Similarly one of the sodium carbonates, Na_2CO_3 , is *mineral*; the other, NaHCO_3 , is *organic*.

The notion that organic substances could only be formed by some mysterious agency, manifested only in organized beings, was finally exploded by the labors of Wöhler and Kolbe. The former obtained urea from ammonium cyanate (1828); while the latter, at a subsequent period, formed acetic acid, using in its preparation only such

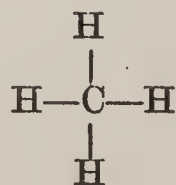
unmistakably mineral substances as coal, sulphur, aqua regia, and water. Since Wöhler's first synthesis, chemists have succeeded not only in making from mineral materials many of the substances previously only formed in the laboratory of nature, but have also produced a vast number of carbon compounds which were previously unknown, and which, so far as we know, have no existence in nature.

At the present time, therefore, we must consider as an organic substance any compound containing carbon, whatever may be its origin and whatever its properties.

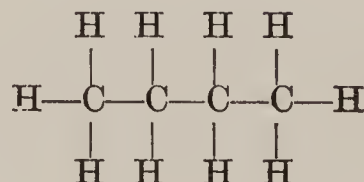
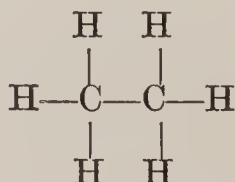
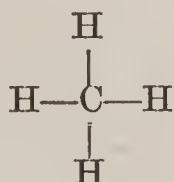
Organic chemistry is, therefore, simply the chemistry of the carbon compounds. In the study of the compounds of the other elements, we have to deal with a small number of substances, relatively speaking, formed by the union with each other of a large number of elements. With the organic substances the reverse is the case. Although compounds have been formed which contain C along with each of the other elements, the great majority of the organic substances are made up of C, combined with a very few other elements; H, O, and N occurring in them most frequently.

It is chiefly in the study of the carbon compounds that we have to deal with **radicals** (see p. 45). Among mineral substances there are many whose molecules consist simply of a combination of two atoms. Among organic substances there is none which does not contain a radical: indeed, organic chemistry has been defined as "**the chemistry of compound radicals.**"

The atoms of carbon possess in a higher degree than those of any other element the power of uniting with each other, and in so doing of interchanging valences. Were it not for this property of the C atoms, we could have but one saturated compound of carbon and hydrogen, CH_4 , or expressed graphically:



There exist, however, a great number of such compounds, which differ from each other by one atom of C and two atoms of H. In these substances the atoms of C may be considered as linked together in a continuous chain, their free valences being satisfied by H atoms, thus:



Homologous Series.—It will be observed that these formulæ differ from each other by CH_2 or some multiple of CH_2 , more or less. In examining numbers of organic substances which are closely related to each other in their properties, we find that we can arrange the great majority of them in series, each term of which differs from the one below it by CH_2 ; such a series is called an **homologous series**. It will be readily understood that such an arrangement in series vastly facilitates the remembering of the composition of organic bodies. In the following table, for example, are given the saturated hydrocarbons, and their more immediate derivatives. At the head of each vertical column is an **algebraic formula**, which is the **general formula** of the entire series below it; n being equal to the numerical position in the series.

HOMOLOGOUS SERIES.

Saturated hydrocarbons, $\text{C}_n\text{H}_{2n+2}$	Alcohols, $\text{C}_n\text{H}_{2n+2}\text{O}$	Aldehydes $\text{C}_n\text{H}_{2n}\text{O}$	Acids, $\text{C}_n\text{H}_{2n}\text{O}_2$	Ketones $\text{C}_n\text{H}_{2n}\text{O}$
CH_4	CH_4O	CH_2O	CO_2H_2
C_2H_6	$\text{C}_2\text{H}_6\text{O}$	$\text{C}_2\text{H}_4\text{O}$	$\text{C}_2\text{O}_2\text{H}_4$
C_3H_8	$\text{C}_3\text{H}_8\text{O}$	$\text{C}_3\text{H}_6\text{O}$	$\text{C}_3\text{O}_2\text{H}_6$	$\text{C}_3\text{H}_6\text{O}$
C_4H_{10}	$\text{C}_4\text{H}_{10}\text{O}$	$\text{C}_4\text{H}_8\text{O}$	$\text{C}_4\text{O}_2\text{H}_8$	$\text{C}_4\text{H}_8\text{O}$
C_5H_{12}	$\text{C}_5\text{H}_{12}\text{O}$	$\text{C}_5\text{H}_{10}\text{O}$	$\text{C}_5\text{O}_2\text{H}_{10}$	$\text{C}_5\text{H}_{10}\text{O}$
C_6H_{14}	$\text{C}_6\text{H}_{14}\text{O}$	$\text{C}_6\text{H}_{12}\text{O}$	$\text{C}_6\text{O}_2\text{H}_{12}$
C_7H_{16}	$\text{C}_7\text{H}_{16}\text{O}$	$\text{C}_7\text{H}_{14}\text{O}$	$\text{C}_7\text{O}_2\text{H}_{14}$
C_8H_{18}	$\text{C}_8\text{H}_{18}\text{O}$	$\text{C}_8\text{H}_{16}\text{O}$	$\text{C}_8\text{O}_2\text{H}_{16}$
C_9H_{20}	$\text{C}_9\text{H}_{20}\text{O}$	$\text{C}_9\text{O}_2\text{H}_{18}$
$\text{C}_{10}\text{H}_{22}$	$\text{C}_{10}\text{H}_{22}\text{O}$	$\text{C}_{10}\text{O}_2\text{H}_{20}$
$\text{C}_{11}\text{H}_{24}$
$\text{C}_{12}\text{H}_{26}$	$\text{C}_{12}\text{O}_2\text{H}_{24}$
$\text{C}_{13}\text{H}_{28}$
$\text{C}_{14}\text{H}_{30}$	$\text{C}_{14}\text{O}_2\text{H}_{28}$

But the arrangement in homologous series does more for us than this. The properties of substances in the same series are similar, or vary in regular gradation according to their position in the series. Thus, in the series of monoatomic alcohols (see table above) each member yields on oxidation, first an aldehyde, then an acid. Each yields a series of compound ethers by the action of acids upon it. The boiling-points of ethylic alcohol and its seven superior homologues are: 78.3° , 97.4° , 116.8° , 137° , 157° , 176° , 195° , from which it will be seen that the boiling-point of any one of them can be determined, with a maximum error of less than 1° , by taking the mean of those of its neighbors above and below. In this way we may predict, to some extent, the properties of a wanting member in a series before its discovery.

The terms of any homologous series must all have the same **con-**

stitution, *i. e.*, their constituent atoms must be similarly arranged within the molecule. (See p. 46.)

Isomerism—Metamerism—Polymerism.—Two substances are said to be isomeric, or to be isomeres of each other, when they have the same percentage composition. If, for instance, we analyze acetic acid, formic aldehyde and methyl formate, we find that each body consists of C, O and H, in the following proportions:

Carbon	40	=	12
Oxygen	53.33	=	16
Hydrogen	6.67	=	2
	<hr/>		<hr/>
	100.00		30

This identity of percentage composition may occur in two ways. The three substances may each contain the same number of each kind of atom in a molecule; or they may contain in their several molecules the same kinds of atoms in multiple proportions. In the above example each substance may have the formula, CH_2O ; or one may have that formula and the others, $\text{C}_2\text{H}_4\text{O}_2$, $\text{C}_3\text{H}_6\text{O}_3$, $\text{C}_4\text{H}_8\text{O}_4$, $\text{C}_5\text{H}_{10}\text{O}_5$, etc.

When two or more substances have the same percentage composition and the same molecular weight they are said to be metameric. When they have the same percentage composition and their molecular weights are simple multiples of the lowest molecular weight represented by that percentage composition, they are said to be polymeric.

Other conditions of isomerism will be considered later (see space isomerism, p. 238, and place isomerism, pp. 260, 337).

In order to determine the composition (the empirical formula) of an organic substance, two factors are therefore necessary: the percentage composition and the molecular weight.

Elementary Organic Analysis.—The first step in an analysis to determine the composition of an organic substance is a qualitative analysis to identify the elements existing in the molecule. This having been done, the quantitative analysis is next in order.

The simplest case is where the substance is a **hydrocarbon**, *i. e.*, a compound of carbon and hydrogen only. The determination of both elements is made in one operation, by taking advantage of the fact that when a compound containing carbon and hydrogen is heated with cupric oxide all the carbon is converted into CO_2 , and all the hydrogen into H_2O . Thus, if $\text{C}_2\text{H}_6\text{O} + 6\text{CuO} = 2\text{CO}_2 + 3\text{H}_2\text{O} + 6\text{Cu}$, 46 parts of alcohol will produce 88 pts. of carbon dioxide and 54 pts. of water.

The apparatus required consists of a tube of difficultly fusible glass, called a combustion tube, about 60 cent. long, drawn out to a point and closed at one end, a "combustion furnace," in which this tube may be heated, and the absorbing apparatus referred to below. A weighed quantity of the substance of

which a "combustion" is to be made (sealed in a small glass bulb if liquid) is placed in the closed end of the combustion tube, *a* Fig. 17, along with the requisite quantity of recently ignited cupric oxide, leaving space for the passage of the gases produced. The tube is then placed in the furnace and its open end connected with a U tube, *b*, filled with fused CaCl_2 , or with fragments of pumice moistened with concentrated H_2SO_4 , whose weight has been determined, and whose purpose it is to absorb the H_2O produced. This first U tube is connected with a "Liebig's bulb" containing a strong solution of KOH , *c*, and this in turn with another U tube in all respects similar to the first, *d*, both *c* and *d* having been previously weighed. The purpose of *c* is to absorb the CO_2 produced, that of *d* to retain water carried over from *c* by the current of gas. The combustion tube is then carefully heated until the evolution of gases ceases, when the closed, drawn-out end of the tube is broken and connected with a gasometer containing pure, dry oxygen, a current of which is passed slowly through the apparatus to bring the last portions of the products of combustion into the absorbing apparatus. Finally the U tubes and the KOH bulb are again weighed. The increase in weight of *b* is the

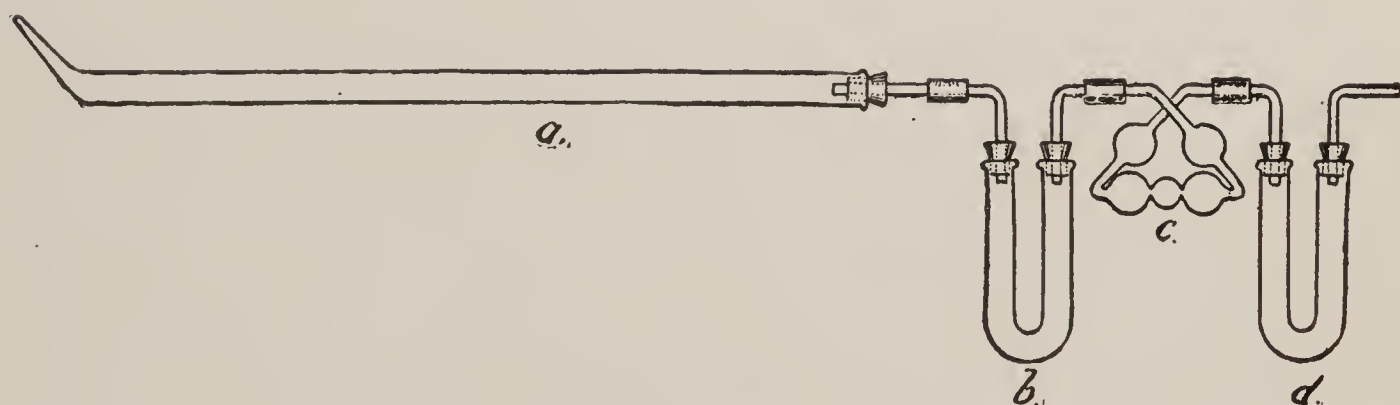


FIG. 17.

weight of H_2O produced, every 9 parts of which represent 1 part of H. The increase in weight of *c* and *d* is the weight of CO_2 produced, every 44 parts of which represent 12 parts of C. If the substance analyzed contains N, Cl, Br or I, a heated column of pure metallic Cu is interposed toward the open end of the combustion tube, to reduce any oxides of N produced to N, and to retain the Cl, Br or I. If the substance contains S, a layer of lead peroxide is similarly placed to retain the S and PbSO_4 .

If the substance consists of C, H and O, the C and H are determined in the manner above described, and the difference between the sum of their weights and that of the substance burnt is the amount of O.

Nitrogen is most readily determined by the **method of Kjeldahl**. A known weight of the substance is dissolved by heating it in concentrated H_2SO_4 . Potassium permanganate is then added until the mixture is green. The N contained in the substance is thus converted into ammonia. The strongly acid liquid is diluted, rendered alkaline by addition of NaOH , and the NH_3 is distilled over into a receiver containing a known quantity of acid. The amount of NH_3 produced is calculated from the amount of acid neutralized, and every 17 parts of NH_3 represent 14 parts of N. In the analysis of nitro- and cyanogen compounds sugar is added, and in that of nitrates, benzoic acid.

Determination of Molecular Weights.—The percentage composition having been determined, the simplest corresponding ratio of the atoms in the molecule is obtained by dividing the percentage of each element by its atomic weight. Thus if analyses are made of formic

aldehyde, acetic acid, methyl formate, lactic acid and glucose, the results in each case will be:

Carbon	40.00	per cent.	$\div 12 = 3.33 = 1$
Hydrogen	6.67	“ “	$\div 1 = 6.67 = 2$
Oxygen	53.33	“ “	$\div 16 = 3.33 = 1$

and the simplest empirical formula of all of the substances mentioned is therefore CH_2O . The molecular weight of formic aldehyde is 30; its formula is therefore $\text{CH}_2\text{O}(12+2+16)$. The molecular weights of acetic acid and of methyl formate are 60: they, therefore, each have the formula $\text{C}_2\text{H}_4\text{O}_2$. The molecular weight of lactic acid is 90 and that of glucose 180: the formula of the former is, therefore, $\text{C}_3\text{H}_6\text{O}_3$, and that of the latter $\text{C}_6\text{H}_{12}\text{O}_6$.

If the substance is one which can be vaporized without decomposition, its molecular weight is derived from its specific gravity as referred to hydrogen. The process for determining the specific gravity now generally adopted is that of Victor Meyer.

Determination of Constitution.—The identity and properties of organic compounds depend not only upon their **composition**, *i.e.*, the number and kind of atoms composing the molecule, but also upon their **constitution**, *i.e.*, the arrangement of the atoms in the molecule (see p. 46). The constitution of a substance is determined by a study of the methods of its formation, of the products of its decomposition, and of the substances produced by the introduction of other elements or groups into its molecule. A statement of the more important principles, and one or two examples, must suffice here, the subject being further developed in the sequel.

The carbon atom is **quadrivalent** in almost all, if not in all its compounds. In the few in which it is considered as bivalent, as in carbon monoxide, CO , and the isonitrils, $(\text{C}_2\text{H}_5)\text{—N}=\text{C}$, the oxygen may be considered to be quadrivalent, and the nitrogen quinquivalent, in which case the carbon would be quadrivalent.

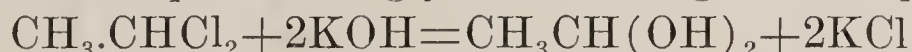
The carbon atoms may unite with each other in three ways: (1) Two carbon atoms may exchange a single valence in their union, forming a hexavalent group, $\equiv \text{C—C} \equiv$; (2) they may unite with exchange of two valences, forming a quadrivalent group, $=\text{C}=\text{C}=$; or, (3) they may unite with exchange of three valences, forming a bivalent group, $\text{—C} \equiv \text{C—}$. These are referred to as **single**, **double** and **treble linkages**, respectively.

Those compounds in which all of the linkages are single, and in which all of the possible valences of the constituent atoms are satisfied are **saturated compounds**. No other atom or radical can be introduced into a saturated molecule except by **substitution**, *i.e.*, by causing the introduced atom or radical to take the place of some other, or others, of equivalent valence, simultaneously removed. Thus, when chloroform (itself a substituted derivative of marsh gas, CH_4) is

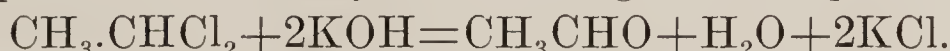
converted into carbon tetrachloride, the remaining hydrogen is removed as hydrochloric acid: $\text{CHCl}_3 + \text{Cl}_2 = \text{CCl}_4 + \text{HCl}$.

Only such substances as contain two carbon atoms doubly or trebly linked, $=\text{C}=\text{C}=$ or $-\text{C}\equiv\text{C}-$, are usually considered as **unsaturated compounds**. Such compounds may be modified both by substitution and by **addition**, *i. e.*, by breaking out the double or treble linkages and the introduction of two new univalents, or one bivalent, for each linkage so liberated. Thus, ethylene yields ethylene chloride by addition: $\text{H}_2\text{C}:\text{CH}_2 + \text{Cl}_2 = \text{ClH}_2\text{C}.\text{CH}_2\text{Cl}$; or, by substitution and addition, carbon hexachloride: $\text{H}_2\text{C}:\text{CH}_2 + 5\text{Cl}_2 = \text{Cl}_3\text{C}.\text{CCl}_3 + 4\text{HCl}$.

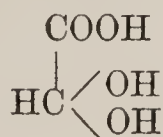
In the reactions referred to above in which chlorine is substituted for hydrogen, it is not only added to the molecule operated upon, but also removes hydrogen by combining with it, and hence two atoms of chlorine are required for each atom of hydrogen removed. Similarly, when O removes H_2 , in oxidations, two atoms of oxygen are required for each two atoms of hydrogen removed, as when alcohol is oxidized to acetic acid: $\text{C}_2\text{H}_6\text{O} + \text{O}_2 = \text{C}_2\text{H}_4\text{O}_2 + \text{H}_2\text{O}$. Consequently in oxidations an even number of hydrogen atoms is always removed. The tendency to the formation of water is so strong that in reactions in which two or more hydroxyl groups should unite with the same carbon atom, water almost invariably splits off and oxygen unites doubly with the carbon. Thus caustic potash does not act upon ethidene chloride to produce a glycol according to the equation:



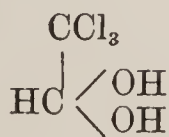
But to produce an aldehyde according to the equation:



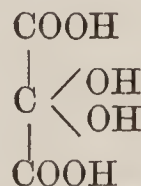
Exceptions to this rule occur when the carbon atom is linked to another carbon atom contained in a highly oxidized or halide group, as in the compounds:



Glyoxalic acid.



Chloral hydrate.



Mesoxalic acid.

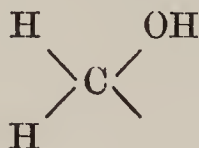
Usually when an atom or group replaces another in a compound it occupies the position vacated by that which is removed, as when alcohol is formed by the action of caustic potash upon ethyl iodide:



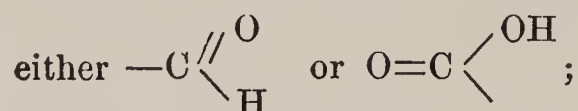
There is an exception to this rule when an unsaturated compound may yield either another unsaturated compound in obedience to the rule or an isomeric saturated compound in violation of it, the more stable saturated compound is formed. Thus the hydration of vinyl bromide, $\text{CH}_2:\text{CHBr}$, does not produce vinyl alcohol, $\text{CH}_2:\text{CHOH}$, but its isomere: aldehyde, CH_3CHO . Indeed, unsaturated compounds

are frequently converted into saturated isomeres by intramolecular transposition of atoms by mere application of heat.

The genesis of ethylic alcohol from the action of caustic potash upon ethyl iodide: $\text{CH}_3\text{CH}_2\text{I} + \text{KOH} = \text{CH}_3\text{CH}_2\text{OH} + \text{KI}$, shows that the alcohol contains the univalent group CH_2OH , or



which, on oxidation, may lose two atoms of hydrogen with formation of either one of the two univalent groups CHO , or COOH ;



which occur in the products of oxidation of ethylic alcohol: aldehyde and acetic acid.

The groups CH_2OH , CHO and COOH , referred to above, are examples of the so-called **characterizing groups** which exist in the molecules of different classes of substances. The following are the more commonly recurring characterizing groups, and the classes of substances in which they occur:

$(\text{CH}_2\text{OH})'$	$= \begin{array}{c} \text{H} \diagdown \\ \text{HO} \diagup \end{array} \text{C} \begin{array}{c} \diagdown \\ \text{H} \end{array}$	in primary alcohols, called <i>methoxyl</i> ,
$(\text{CHOH})''$	$= \begin{array}{c} \text{H} \diagdown \\ \text{HO} \diagup \end{array} \text{C} =$	“ secondary alcohols,
$(\text{COH})'''$	$= :\text{C}.\text{OH}$	“ tertiary alcohols,
$(\text{CHO})'$	$= \text{O}=\text{C} \begin{array}{c} \diagup \\ \text{H} \end{array}$	“ aldehydes,
$(\text{CO})''$	$= \text{O}:\text{C}:$	“ ketones, called <i>carbonyl</i> ,*
$(\text{COOH})'$	$= \text{O}=\text{C} \begin{array}{c} \diagup \\ \text{OH} \end{array}$	“ acids, called <i>carboxyl</i> ,
$(\text{SO}_2\text{OH})'$	$= \begin{array}{c} \text{O} \diagdown \\ \text{O} \diagup \end{array} \text{S} \begin{array}{c} \diagdown \\ \text{OH} \end{array}$	“ sulphonic acids,
$(\text{SO}_2)''$	$= \begin{array}{c} \text{O} \diagdown \\ \text{O} \diagup \end{array} \text{S} =$	“ sulphones,
$(\text{NH}_2)'$	$= \text{H}_2:\text{N}.$	“ amido compounds,
$(\text{NH})''$	$= \text{H}:\text{N}:$	“ imido compounds,
$(\text{NO}_2)'$	$= \begin{array}{c} \text{O} \diagdown \\ \text{O} \diagup \end{array} \text{N}-$	“ nitro compounds,
$(\text{NO})'$	$= \text{O}:\text{N}.$	“ nitroso compounds.

Nomenclature of Organic Compounds.—The vast number and great variety of structure of organic compounds make it difficult to

* This group also exists in other compounds, as in the aldehydes and acids in the manner indicated in the text, and in compounds, such as carbonyl chloride, COCl_2 , urea, $\text{NH}_2.\text{CO}.\text{NH}_2$, etc.

devise a system of nomenclature which will apply to the more complex derivatives without producing names which are most complicated and difficult of pronunciation. Indeed, in view of the constantly increasing number of carbon compounds, no complete system of nomenclature is as yet possible. The most recent attempt to formulate one is that of the Geneva Convention of 1892. In this system the names of the hydrocarbons serve as the roots from which the names of their derivatives are constructed by the addition of syllables indicating the function (see p. 208) of the substance. Thus the alcohols are indicated by the syllable *ol*, the aldehydes by *al*, the ketones by *on*, and the acids by the word *acid*. The "Geneva" name of ethylic alcohol would be *ethanol*, that of acetic aldehyde *ethanal* and that of acetic acid *ethan-acid*. These names have not come into general use.

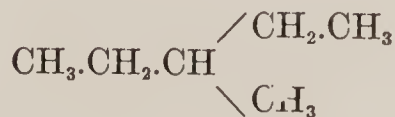
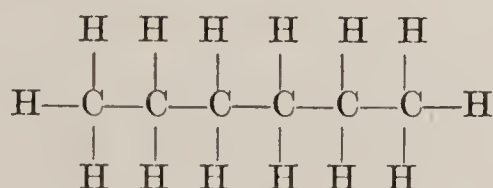
In the nomenclature generally followed the name of a substance is made up of the name of that of the class, or "function," to which the substance belongs, as *acid*, *alcohol*, *ketone*, *ester*, etc., to which is added a qualifying word derived from the origin of the body, as *lactic acid*, *acetic acid*, etc., or from its composition, as *methylic alcohol*, *ethylic ether*, etc., and the names of any radicals which have been introduced into the molecule of the parent compound. Thus the name of the substance $\text{COOH} \cdot \text{CH}_2(\text{NH} \cdot \text{CH}_3)$ is *methyl-amido-acetic acid*, in which "*acetic acid*" indicates that it is derived from acetic acid, $\text{COOH} \cdot \text{CH}_3$, the syllable *amido* that NH_2 has been substituted for H in the CH_3 of the acid, and *methyl* that CH_3 has been substituted for H in NH_2 .

The names of the univalent radicals terminate in *yl*, as *methyl* $(\text{CH}_3)'$, *ethyl* $(\text{C}_2\text{H}_5)'$, *acetyl* $(\text{C}_2\text{H}_3\text{O})'$, etc. Those of bivalent radicals terminate in *ene*, as *methylene*, $(\text{CH}_2)''$, *ethidene* $(\text{C}_2\text{H}_4)''$, etc., and those of the trivalent radicals in *enyl*, or in *ine*, as *methenyl* or *methine* $(\text{CH})'''$, *ethenyl* or *ethine* $(\text{C}_2\text{H}_3)'''$, etc.

Classification of the Carbon Compounds.—The hydrocarbons, consisting of carbon and hydrogen only, constitute the framework of the classification adopted, all other carbon compounds being considered as derivable from the hydrocarbons by substitution or by addition.

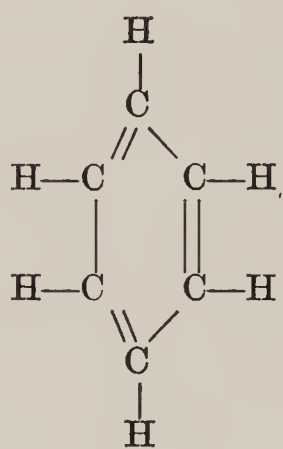
Carbon compounds are divided into two great classes, differentiated by the manner in which the carbon atoms are linked together:

A. OPEN CHAIN COMPOUNDS, also called *acyclic*, *fatty*, or *aliphatic* compounds. In these compounds the carbon atoms are attached to each other in an open or arborescent chain, in which two or more carbon atoms are linked to but one other carbon atom, as in the compounds:

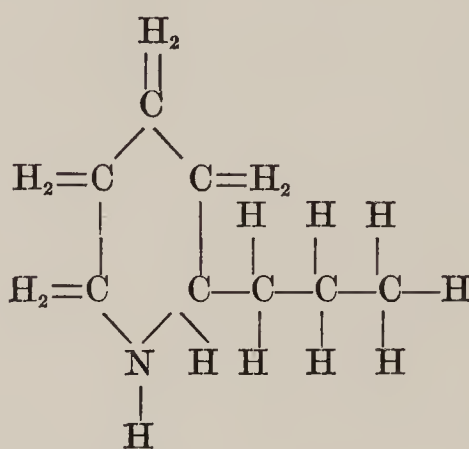


* In the hydrocarbons of this class the number of hydrogen atoms, or this number, plus the number of univalent atoms that can be introduced into the molecule by addition, is equal to twice the number of carbon atoms plus two.

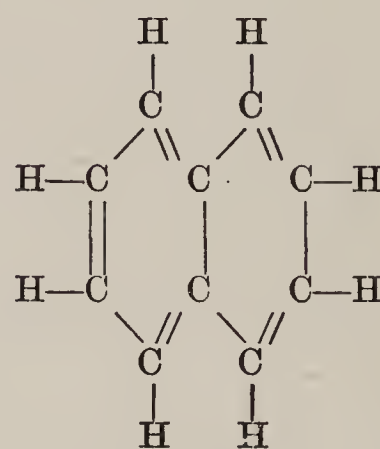
B. CLOSED CHAIN COMPOUNDS, also called *cyclic* or *aromatic* compounds. These compounds contain one or more closed *chains*, *rings*, or *nuclei* in which each carbon atom is linked to at least two other carbon atoms, or their equivalent, as in the compounds:



Benzene.



Coniine



Naphthalene.

The closed chain compounds are subdivided into two classes:

I. *Carbocyclic compounds*, in which the ring or rings consist of carbon atoms exclusively, as in benzene and naphthalene, and

II. *Heterocyclic compounds*, in which atoms of elements other than carbon enter into the composition of the ring, as in coniine.

OPEN CHAIN, ALIPHATIC, ACYCLIC OR FATTY COMPOUNDS.

HYDROCARBONS.

Six series are known :

A. Methane, or Paraffin Series. These are saturated compounds and have the algebraic formula, C_nH_{2n+2} . Their names terminate in "ane," *e.g.*, Butane, $CH_3.CH_2CH_2.CH_3$.

B. Olefine Series, containing two doubly-linked carbon atoms. General formula C_nH_{2n} . Their names terminate in "ene," *e.g.*, Butene, $CH_2:CH.CH_2CH_3$.

C. Acetylene Series, containing two trebly-linked carbon atoms. Algebraic formula, C_nH_{2n-2} . Their names terminate in "ine," *e.g.*, Propine, $CH:C.CH_3$.

D. Diolefine Series, containing two pairs of doubly-linked carbon atoms. Algebraic formula, C_nH_{2n-2} , isomeric with the members of the acetylene series. Their names terminate in "diene," *e.g.*, Propadiene, $CH_2:C:CH_2$. Trienes are also known, containing three pairs of doubly-linked carbon atoms, *e.g.*, Octatriene, $CH_2:CH.CH_2.CH_2.CH:CH.CH:CH_2$.

E. Olefine-acetylene Series, containing both doubly- and trebly-linked carbon atoms. General formula, C_nH_{2n-4} . Their names terminate in "one," *e.g.*, Butone, $H_2C:CH.C:CH$.

F. Diacetylene Series, containing two pairs of trebly-linked carbon atoms. Algebraic formula, C_nH_{2n-6} . Their names are constructed by prefixing the syllable "di" to the name of the hydrocarbon of series C, from which they are derivable by fusion and elimination of H_2 or its equivalent, *e.g.*, Diacetylene, $HC:C.C:CH$. The sixth terms, of which there are two isomeres: Dipropargyl, $HC:C.CH_2.CH_2.C:CH$, and Dimethyl diacetylene, $H_3C.C:C.C:C.CH_3$, are isomeric with benzene, the most important of the closed chain hydrocarbons.

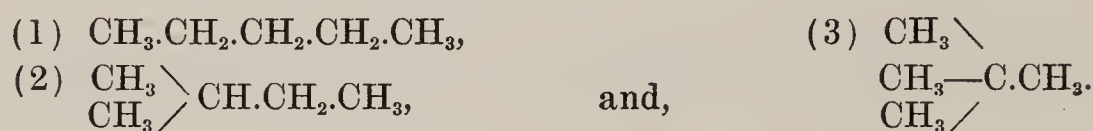
SATURATED COMPOUNDS—METHANE SERIES.

The hydrocarbons of the methane series are saturated, as are also most of the compounds derived from them. There are, however, certain of their derivatives, classed here for convenience, which contain either a doubly-linked oxygen atom (the aldehydes and ketones) or a trivalent nitrogen atom (the amines, amides, etc.), which form *addition products* and are, therefore, strictly speaking, *unsaturated* compounds.

HYDROCARBONS.

The saturated hydrocarbons at present known extend in unbroken series from methane, CH_4 , to tetracosane, $\text{C}_{24}\text{H}_{50}$; and above that some members are known as high as dimyricyl, $\text{C}_{60}\text{H}_{122}$. The algebraic formula of the series is $\text{C}_n\text{H}_{2n+2}$. They are called **paraffins** because of their great stability (*parum*=little, *affinis*=affinity); and also **alkanes**. They are also considered as the **hydrides** of the alcoholic radicals, $\text{C}_n\text{H}_{2n+1}$, methyl, ethyl, etc., which are called **alkyls**.

In the higher terms of the series, above the third, there exist two or more isomeres, increasing progressively in number with an increasing number of carbon atoms. Thus there are three having the empirical formula, C_5H_{12} :



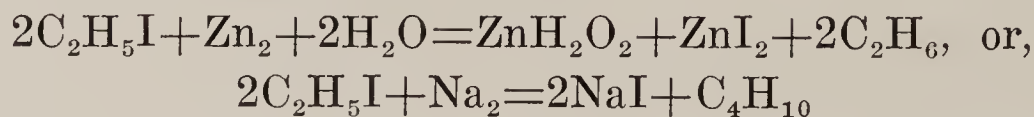
Hydrocarbons and their derivatives having the “unbranched” structure shown in formula (1) above, are designated as **normal** compounds; those derived from (2) are called **iso** compounds; and those derived from (3) **meso** compounds.

The number of possible isomeres increases rapidly with an increasing number of carbon atoms. It has been calculated that the number of possible isomeres with increasing values of n are as follows:

$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
1	1	1	2	3	5
$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 11$	$n = 12$
9	18	35	75	159	357

Many of these hydrocarbons exist in nature, in petroleum, and in the gases accompanying it. They may be produced by the following **general reactions**:

(1) By the action of finely-divided zinc, silver or copper, or of sodium either alone, at elevated temperatures, or in the presence of H_2O , upon the corresponding iodides:



(2) By electrolysis of the corresponding fatty acid:



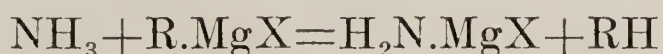
(3) By heating the salts of the fatty acids with soda-lime:



(4) By the action of the organo-zincic derivative upon the iodide of the alcoholic radical, or upon the corresponding olefine iodide.

(5) By the action of highly concentrated hydriodic acid at 275° – 300° upon hydrocarbons of the ethene and ethine series, upon alcohols, amines, etc. This is a method of hydrogenation applicable in many other cases.

(6) By the action of alkyl magnesium halides upon ammonia, amines, or phenylhydrazine:



(7) By the destructive distillation of many organic substances.

General Properties.—They are gaseous, liquid, or solid, and have sp. gr. and boiling points increasing with the number of C atoms. The first four members are gaseous at the ordinary temperature, those above $\text{C}_{15}\text{H}_{32}$ are crystalline solids; the intermediate ones are colorless liquids. They are lighter than H_2O , neutral, insoluble in H_2O , soluble in alcohol, ether, and in liquid hydrocarbons. Their odor is faint and not unpleasant.

Chlorine and bromine decompose them, with formation of products of substitution. They are inflammable and burn with a luminous flame. Nitric acid forms nitro-derivatives with the higher terms.

Methyl Hydride—Methane—Marsh-gas—Fire-damp— CH_4 —16— is given off in swamps as a product of decomposition of vegetable matter, in coal mines, and in the gases issuing from the earth in the vicinity of petroleum deposits. It is also formed during putrefaction of protein bodies and fermentation of carbohydrates. From these origins it exists in intestinal gases, sometimes to the extent of 26.5 per cent. Coal-gas contains it in the proportion of 36–50 per cent.

Preparation.—It may be prepared by strongly heating a mixture of sodium acetate with sodium hydroxide and quick-lime:



Its complete synthesis, which is of theoretic interest, may be effected in several ways: (1) Carbon disulphide is first produced by passing vapor of sulphur over coal, heated to redness: $\text{C} + \text{S}_2 = \text{CS}_2$. This may either be passed, along with hydrogen sulphide, over red-hot copper, when: $\text{CS}_2 + 2\text{H}_2\text{S} + 8\text{Cu} = \text{CH}_4 + 4\text{Cu}_2\text{S}$, or, (2) it may be converted into carbon tetrachloride by the reaction: $\text{CS}_2 + 3\text{Cl}_2 = \text{CCl}_4 + \text{S}_2\text{Cl}_2$; and this reduced by nascent hydrogen: $\text{CCl}_4 + 4\text{H}_2 = \text{CH}_4 + 4\text{HCl}$. (3) Carbon monoxide, prepared by heating carbon in a limited quantity of air, is reduced by hydrogen when the two are treated with the induced electric current: $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$. (4) Aluminium carbide is decomposed by water according to the equation: $\text{C}_3\text{Al}_4 + 12\text{H}_2\text{O} = 3\text{CH}_4 + 2\text{Al}_2(\text{HO})_6$.

Properties.—It is a colorless, odorless, tasteless gas; very sparingly soluble in H_2O ; sp. gr. 0.559A. At high temperatures, it is decomposed into C and H. It burns in air with a pale yellow flame. Mixed with air or O it explodes violently on contact with flame, pro-

ducing water and carbon dioxide; the latter constituting the **after-damp** of miners. It is not affected by Cl in the dark, but, under the influence of diffuse daylight, one or more of the H atoms are displaced by an equivalent quantity of Cl. In direct sunlight the substitution is accompanied by an explosion.

Petroleum.—Crude petroleum varies in color from a faintly yellowish tinge to a dark brown, nearly black, with greenish reflections. The lighter-colored varieties are limpid, and the more highly colored of the consistency of thin syrup. The sp. gr. varies from 0.74 to 0.92. Crude petroleum consists of normal paraffins (the lowest terms of the series being found in the gases accompanying petroleum and held in solution by the oil under the pressure it supports in natural pockets), besides hydrocarbons of the olefine, paraffin, and benzene series. They also contain varying quantities of sulphur compounds, which communicate a disgusting odor to some oils.

The crude oil is highly inflammable, usually highly colored, and is prepared for its multitudinous uses in the arts by the processes of distillation and refining. The products of lowest boiling point are usually consumed, but are sometimes condensed.

The principal products of petroleum are: **Cymogene**, boils at 0°, used in ice machines; **Rhigolene**, a highly inflammable liquid, sp. gr. about 0.60, boils at about 20°, used to produce cold by its rapid evaporation. **Petroleum ether**, boils at 40°–50°, used as a solvent. **Gasolene**, boils from 45° to 76°, used as a fuel and for the manufacture of “air gas.” **Naphtha**, divided into three grades, C, B, and A, boils from 82.2° to 148.8°, used as a solvent for fats, etc., and in the manufacture of “water gas.” Sometimes called “safety oil.” **Benzine**, or **benzolene**, boils from 148° to 160°, used as a solvent in making paints and varnishes. The most important product of petroleum is that portion which distils between 176° and 218°, and which constitutes **kerosene** and other oils used for burning in lamps. An oil to be safely used for burning in lamps should not “flash,” or give off inflammable vapor, below 37.4°, and should not burn at temperatures below 149°. The better grades of kerosene have a flash point of from 45° to 65°.

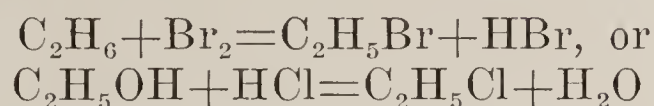
From the residue remaining after the separation of the kerosene, many other products are obtained. **Lubricating oils**, of too high boiling-point for use in lamps. **Paraffin**, a white, crystalline solid, fusible at 45°–65°, which is used in the arts for a variety of purposes formerly served by wax, such as the manufacture of candles. In the laboratory it is very useful for coating the glass stoppers of bottles, and for other purposes, as it is not affected by acids or by alkalis. It is odorless, tasteless, insoluble in H₂O and in cold alcohol; soluble in boiling alcohol and in ether, fatty and volatile oils and mineral oils. It is also obtained by the distillation of certain varieties of coal, and is found in nature in **fossil wax** or **ozocerite**.

The products known as **vaseline**, **cosmoline**, etc., are mixtures of paraffin and the heavier petroleum oils. Their consistency depends upon the relative proportion of the higher paraffins, of increasing fusing-point, which they contain, from the oily **petrolatum liquidum** (U. S. P.), to the hard **petrolatum** or **petrolatum album** (U. S. P.). Like petroleum itself, its various commercial products are not definite compounds, but mixtures of the hydrocarbons of this series.

HALOID DERIVATIVES OF THE PARAFFINS.

By the action of Cl or Br, upon the paraffins, or by the action of HCl, HBr or HI upon the corresponding hydroxides, the monohydric

alcohols, compounds are obtained in which one of the H atoms of the hydrocarbon has been replaced by an atom of Cl, Br or I:



Or they are more readily obtained by the action of the phosphorus halides, or of the halogen in presence of phosphorus upon the monohydric alcohols:

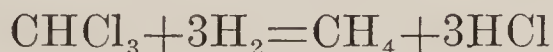


These monohalogen paraffins, or haloid ethers, or haloid esters, or alkyl halides, may also be considered as the chlorides, etc., of the alcoholic radicals, methyl, etc.

When Cl is allowed to act upon CH_4 , it replaces a further number of H atoms until finally carbon tetrachloride, CCl_4 , is produced. Considering marsh gas as methyl hydride, $\text{CH}_3.\text{H}$, the first product of substitution is methyl chloride, CH_3Cl ; the second monochloromethyl chloride, $\text{CH}_2\text{Cl}.\text{Cl}$; the third dichlormethyl chloride, or chloroform, $\text{CHCl}_2.\text{Cl}$; and the fourth carbon tetrachloride, CCl_4 .

Similar derivatives are formed with Br and I, and with the other hydrocarbons of the series.

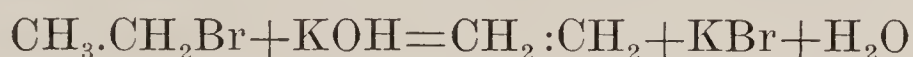
Nascent hydrogen reduces all of the halogen derivatives to the parent hydrocarbons:



These compounds are of great service for the introduction of their alkyls into other molecules. Thus, benzene and methyl chloride form methyl benzene:



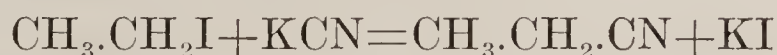
Caustic potash or soda in alcoholic solution splits off the halogen and water, with formation of an unsaturated hydrocarbon:



Heated with aqueous potash the haloid esters produce the corresponding alcohols:



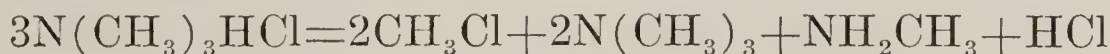
Heated with alcoholic solution of potassium cyanide at 100° , the haloid esters produce the alkyl cyanides:



They also combine with ammonia to form amines:



Methyl Chloride— CH_3Cl —50.5—is a colorless gas, slightly soluble in H_2O , and having a sweetish taste and odor. It is prepared commercially by heating trimethylammonium chloride (obtained by distilling beet sugar molasses):



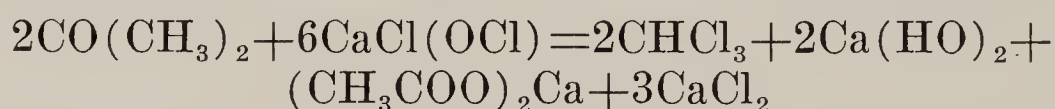
It may be condensed to a liquid which boils at -22° , in which form it is used in ice machines, as a spray in neuralgia, and as an anesthetic; for the latter uses either alone or mixed with CHCl_3 , $\text{C}_4\text{H}_{10}\text{O}$, or $\text{C}_2\text{H}_5\text{Cl}$. It burns with a greenish flame.

Dichlormethane — Methene chloride — Methylene chloride — Monochlormethyl chloride— CH_2Cl_2 —85—is obtained by the action of Cl upon CH_4 , and by the reduction of CHCl_3 by nascent hydrogen.

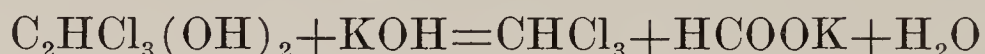
It is a colorless, oily liquid; boils at 40° ; sp. gr. 1.36; its odor is similar to that of chloroform; it is very slightly soluble in H_2O and is not inflammable. It has been used as an anesthetic, but has been discarded as being less safe than chloroform.

Trichlormethane—Methenyl chloride—Dichlormethyl chloride—Chloroform—Chloroformum (U. S. P.)— CHCl_3 —119.5.

Chloroform is manufactured by the action of bleaching powder upon acetone, the reaction being expressed by the equation:



It is best obtained pure by heating chloral hydrate with an alkali:



It is a colorless, volatile liquid, having a strong, agreeable, ether-eal odor, and a sweet taste; sp. gr. 1.497; very sparingly soluble in H_2O ; miscible with alcohol and ether in all proportions; boils at 60.8° . It is a good solvent for many substances insoluble in H_2O , such as phosphorus, iodine, fats, resins, caoutchouc, gutta-percha and the alkaloids.

It ignites with difficulty, but burns from a wick with a smoky, red flame, bordered with green. It is not acted on by H_2SO_4 , except after long contact, when HCl is given off. In direct sunlight Cl converts it into CCl_4 and HCl . The alkalies in aqueous solution do not act upon it, but when heated with them in alcoholic solution, it is decomposed with formation of chloride and formate of the alkaline metal:



When perfectly pure it is not altered by exposure to light; but if it contains compounds of N , even in very minute quantity, it is gradually decomposed by solar action into HCl , Cl and other substances. When used as an anesthetic chloroform should not be colored by agitation with concentrated, colorless sulphuric acid, and should color the latter only faintly yellow, or not at all; and when it is evaporated the remaining film of moisture should have no taste or odor other than those of chloroform.

Analytical Characters.—(1) Add a little alcoholic solution of potash and 2–3 drops of aniline and warm: the disagreeable odor of isobenzonitrile (*q.v.*) is produced. (2) Vapor of CHCl_3 , when passed through a red-hot tube, is decomposed with formation of HCl and

Cl, the former of which is recognized by the production of a white ppt., soluble in ammonium hydroxide, in an acid solution of silver nitrate. This test does not afford reliable results when the substance tested contains a free acid and chlorides. (3) Dissolve about 0.01 gm. of β naphthol in a small quantity of KOH solution, warm, and add the suspected liquid; a blue color is produced. (4) Add about 0.3 gm. resorcinol in solution, and 3 gtt. NaOH solution and boil strongly; in the presence of CHCl_3 a red color is produced. But the liquid exhibits no fluorescence (p. 232).

Toxicology.—The action of chloroform varies as it is taken by the stomach or by inhalation. In the former case, owing to its insolubility, but little is absorbed, and the principal action is the local irritation of the mucous surfaces. Recovery has followed a dose of four ounces, and death has been caused by one drachm, taken into the stomach. Chloroform vapor acts much more energetically, and seems to owe its potency for evil to its paralyzing influence upon the respiratory nerve centers, and upon the cardiac ganglia. While persons suffering from heart disease are particularly susceptible to the paralyzing effect of chloroform vapor, there are many cases recorded of death from the inhalation of small quantities, properly diluted, in which no heart lesion was found upon a post-mortem examination. Chloroform is apparently not altered in the system.

No chemical *antidote* for chloroform is known. When it has been swallowed, stomach-lavage and emetics are indicated; when taken by inhalation, a free circulation of air should be established about the face; artificial respiration and the application of the induced current to the sides of the neck and epigastrium should be resorted to.

Carbon Tetrachloride— CCl_4 —154—is formed by the prolonged action, in sunlight, of Cl upon CH_3Cl or CHCl_3 ; or more rapidly, by passing Cl, charged with the vapor of carbon disulphide, through a red-hot tube, and purifying the product.

It is a colorless, oily liquid, insoluble in H_2O ; soluble in alcohol and in ether; sp. gr. 1.56; boils at 78° . Its vapor is decomposed at a red heat into a mixture of the **dichloride**, C_2Cl_4 , **trichloride**, C_2Cl_6 , and free Cl.

Tribromomethane—*Dibromomethyl bromide*—*Methenyl bromide*—**Bromoform**— $\text{CHBr}_2\cdot\text{Br}$ —253—is prepared by gradually adding Br to a cold solution of KOH in methyl alcohol until the liquid begins to be colored; and rectifying over CaCl_2 .

A colorless, aromatic, sweet liquid; sp. gr. 2.13; boils at 150° – 152° ; solidifies at -9° ; sparingly soluble in H_2O ; soluble in alcohol and ether. Boiled with alcoholic KOH it is decomposed in the same way as in CHCl_3 .

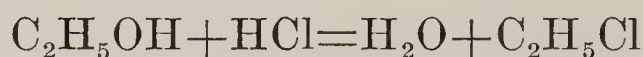
Its physiological action is similar to that of CHCl_3 . It occurs as an impurity of commercial Br, accompanied by **carbon tetrabromide**, CBr_4 .

Triiodomethane—*Diiodomethyl iodide*—*Methenyl iodide*—**Iodoform**—**Iodoformum**, (U. S. P.)— CHI_2I —394.—Formed like CHCl_3 ,

and CHBr_3 , by the combined action of KOH and the halogen upon alcohol; it is also produced by the action of I upon a great number of organic substances, and is usually prepared by heating a mixture of alkaline carbonate, H_2O , I and ethylic alcohol, and purifying the product by recrystallization from alcohol. It is also produced from acetone by making a solution containing 50 gm. KI , 6 gm. acetone, and 2 gm. NaOH in 2 L. H_2O and gradually adding a dilute solution of KClO_3 . Triiodoaldehyde and triiodoacetone are formed as intermediate products.

Iodoform is a solid, crystallizing in yellow, hexagonal plates, which melt at 120° . It may be sublimed, a portion being decomposed. It is insoluble in water, acids and alkaline solutions; soluble in alcohol, ether, carbon disulphide, and the fatty and essential oils; the solutions, when exposed to the light, undergo decomposition and assume a violet-red color. It has a sweet taste, and a peculiar, penetrating odor, resembling, when the vapor is largely diluted with air, that of saffron. When heated with potash a portion is decomposed into formate and iodide, while another portion is carried off unaltered with the aqueous vapor. It contains 96.7% of its weight of iodine.

Ethyl Chloride—*Hydrochloric or muriatic ether*— $\text{C}_2\text{H}_5\text{Cl}$ —64.5.—A colorless, ethereal liquid; boils at 11° ; obtained by passing gaseous HCl through ethylic alcohol to saturation, and distilling over the water-bath:



It is now used to produce cold by spraying. The liquid and vapor are readily inflammable.

Ethyl Bromide *Hydrobromic ether*— $\text{C}_2\text{H}_5\text{Br}$ —109—A colorless, ethereal liquid; boils at 40.7° , obtained by the combined action of P and Br on ethylic alcohol. It has been used as an anesthetic in minor surgery.

Ethyl Iodide—*Hydriodic ether*— $\text{C}_2\text{H}_5\text{I}$ —156—is prepared by placing absolute alcohol and P in a vessel surrounded by a freezing mixture and gradually adding I . When the action has ceased, the liquid is decanted, distilled over the water-bath and the distillate washed and rectified. It is a colorless liquid; boils at 72.2° ; has a powerful, ethereal odor; burns with difficulty. It is largely used in the aniline industry.

OXIDATION PRODUCTS OF THE PARAFFINS.

Many important and varied classes of compounds are derivable from the paraffins by oxidation:

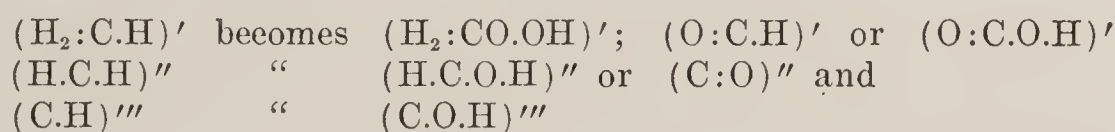
One of these may be considered as derived * from the hydrocarbon by the introduction of an oxygen atom between two of its hydrocarbon groups. Thus from the hydrocarbon butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ we may derive the oxides CH_3 .

* Note: The words "*derived*" and "*obtained*" are not used synonymously. One substance is said to be derived from another when there is such relation between their molecular structures that the constitutional formula of the more complex may be produced from that of the more simple by substitution. A method of obtention is a process by which a substance is manufactured, and does not imply any relation between the molecular structures of the product and parent, although such may, and very frequently does, exist.

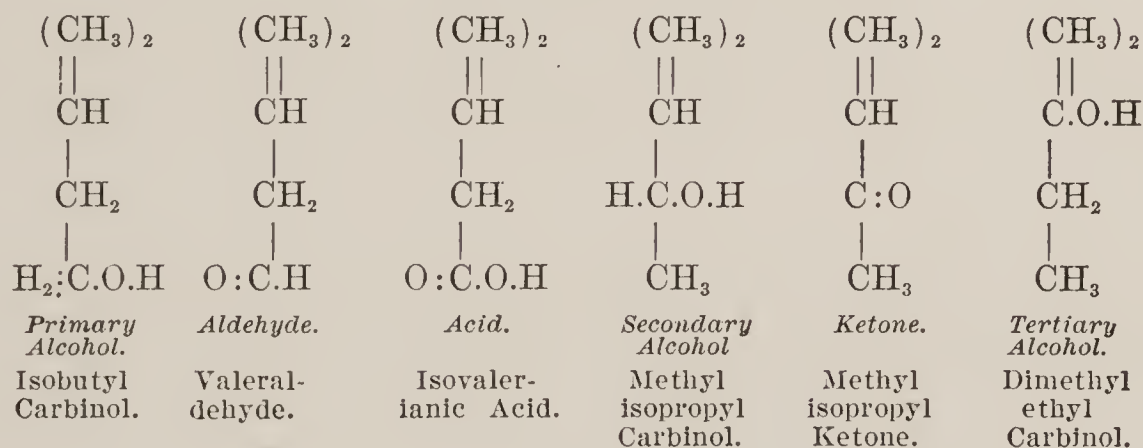
$\text{CH}_2.\text{O}.\text{CH}_2\text{CH}_3$ and $\text{CH}_3.\text{O}.\text{CH}_2.\text{CH}_2.\text{CH}_3$. These are the true oxides of the alkyls, and are known as **simple** and **mixed ethers**, according as the oxygen atom is symmetrically or unsymmetrically introduced or two oxygen atoms may be thus introduced; as in the formals (p. 232): $\text{CH}_3\text{O}.\text{CH}_2\text{O}.\text{CH}_3$. Or, in other classes of compounds, an oxygen atom may be interpolated as in the ethers, and one or more of the hydrocarbon groups may be also oxidized. In this manner compounds of very diverse nature are derived: **Esters**, such as ethyl acetate, $\text{CH}_3.\text{CO}.\text{O}.\text{CH}_2.\text{CH}_3$; **acid anhydrides**, or **acidyl oxides**, such as acetic anhydride, $\text{CH}_3.\text{CO}.\text{O}.\text{CO}.\text{CH}_3$; certain **acids**, such as diglycollic acid, $\text{COOH}.\text{CH}_2.\text{O}.\text{CH}_2.\text{COOH}$, and certain **dihydric alcohols**, such as diethylene glycol, $\text{CH}_2\text{OH}.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_2\text{OH}$. It will be more convenient to consider these several classes of compounds after having discussed the other oxidation products.

Four other classes are more closely related to each other. They may be considered as being derived from the hydrocarbons in one of two ways; either

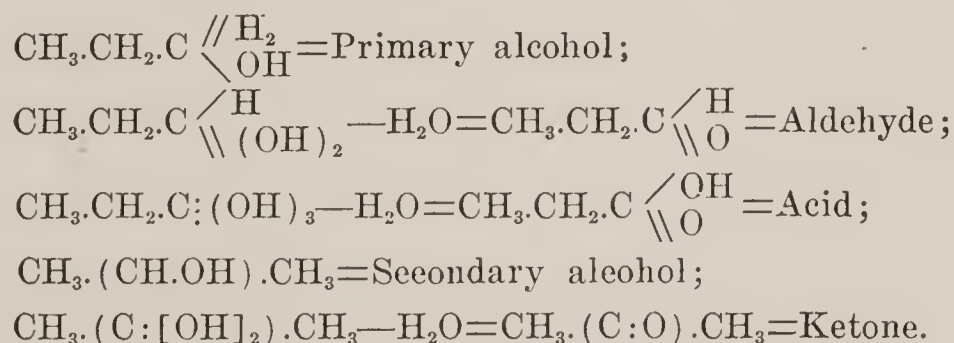
(1) By the interpolation or substitution, or both, of an oxygen atom or atoms in one of the groups CH_3 , CH_2 , or CH of the parent hydrocarbon (see formulæ on p. 210). Thus:



and by the oxidation of a single group in the hydrocarbon: isopentane; $(\text{CH}_3)_2:\text{CH}.\text{CH}_2\text{CH}_3$ the following products may be obtained:

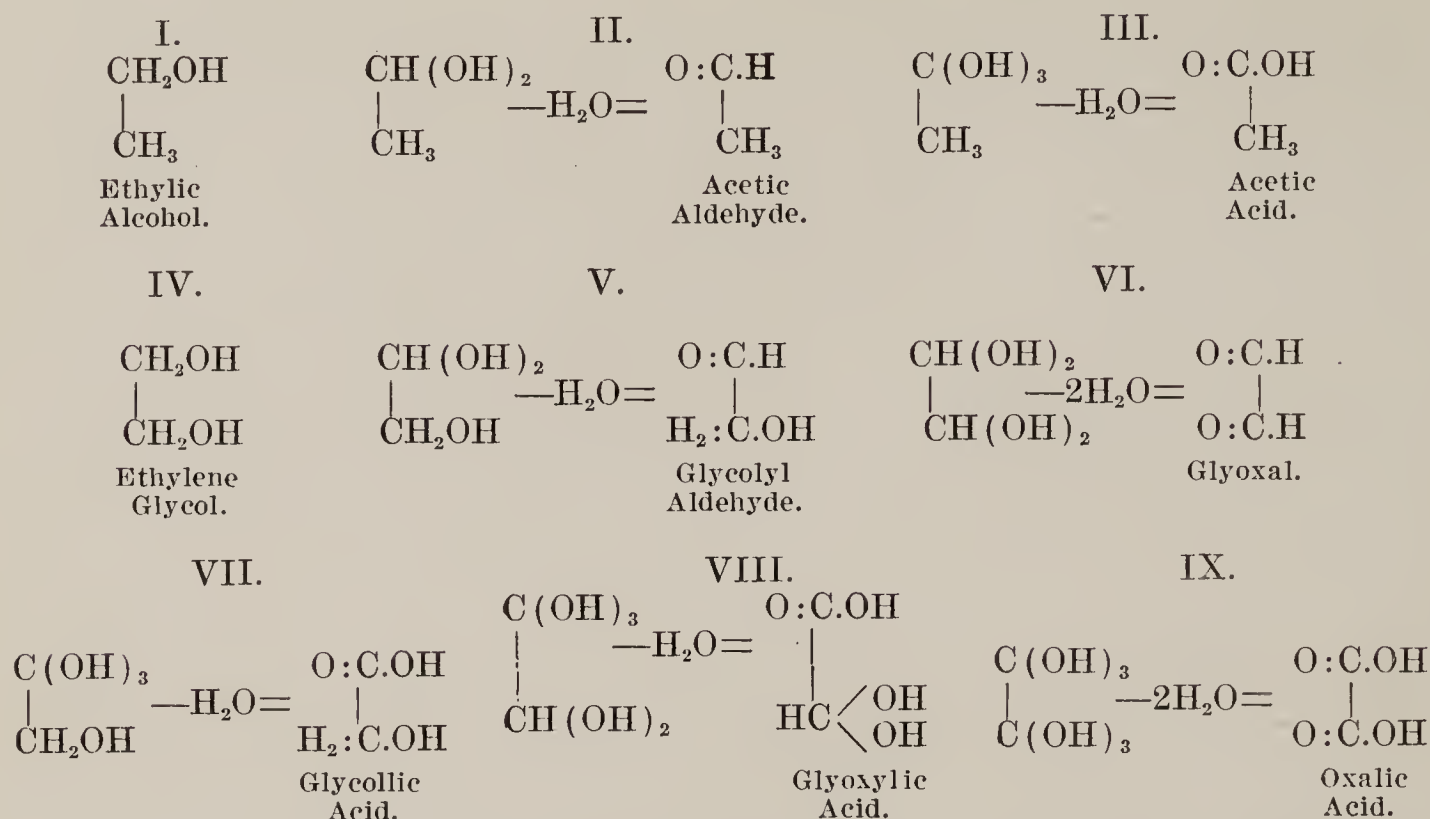


(2) Or these compounds may be considered as produced by the substitution of hydroxyls (OH), for one or more of the hydrogen atoms of the hydrocarbon, it being remembered that when a substance is thus produced in which two hydroxyls are attached to the same carbon atom, water separates, except under the circumstances referred to on page 197. Thus from the hydrocarbon: propane, $\text{CH}_3.\text{CH}_2.\text{CH}_3$, the following products may be derived by substitution in a single hydrocarbon group:



When the number of hydroxyls substituted in each hydrocarbon group exceeds one, the number of derivatives increases rapidly with an increasing num-

ber of C atoms in the parent hydrocarbon. Thus the second term of the series, $\text{CH}_3.\text{CH}_3$, yields nine derivatives:



There are twenty-nine possible derivatives of the third hydrocarbon, $\text{CH}_3.\text{CH}_2.\text{CH}_3$.

The four classes of oxidation products under consideration are:

A. The alcohols, subdivided into (a) *Primary*, containing the group $-\text{C} \begin{array}{l} // \text{H}_2 \\ \backslash \text{OH} \end{array}$; (b) *Secondary*, containing the group $=\text{C} \begin{array}{l} \swarrow \text{H} \\ \searrow \text{OH} \end{array}$; and (c) *Tertiary*, containing the group $\equiv \text{C}:\text{OH}$;

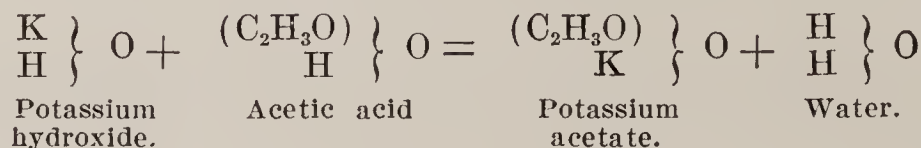
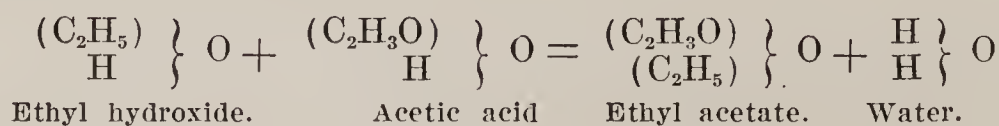
B. The aldehydes, containing the group $-\text{C} \begin{array}{l} // \text{O} \\ \backslash \text{OH} \end{array}$;

C. The ketones, containing the group $=\text{C}=\text{O}$; and

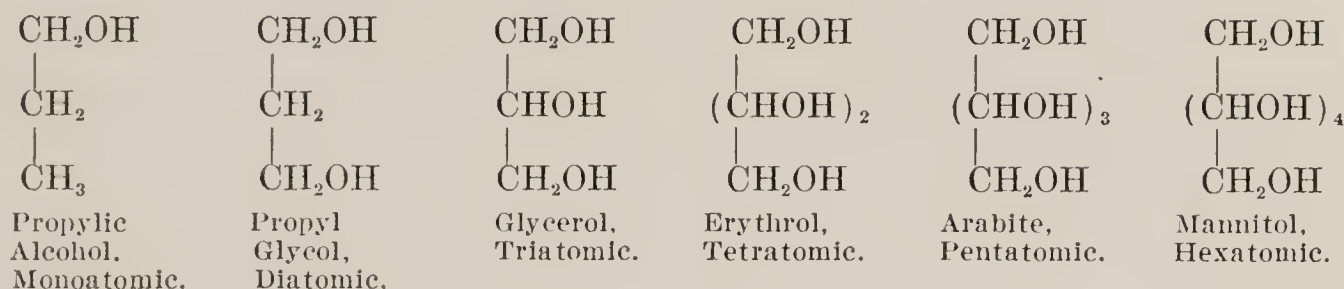
D. The carboxylic acids, containing the group **carboxyl**: $-\text{C} \begin{array}{l} // \text{O} \\ \backslash \text{OH} \end{array}$

ALCOHOLS—HYDROCARBON HYDROXIDES.

These substances are mainly characterized by their power of entering into double decomposition with acids to form neutral compounds, called **esters**, water being at the same time formed at the expense of both alcohol and acid. They are the hydroxides of hydrocarbon radicals, the alkyls, and as such resemble the metallic hydroxides, while the esters are the counterparts of the metallic salts:



Or they may be regarded as substances derived from the hydrocarbons by the substitution of one or more hydroxyls for one or more hydrogen atoms. Alcohols containing one OH are designated as **monoatomic** or **monohydric**; those containing two OH groups are **diatomic** or **dihydric**, etc.:



MONOATOMIC, OR MONOHYDRIC ALCOHOLS.

Beginning with the third member of the series, an increasing number of isomeres of the higher terms are known.

I. Some of these alcohols yield on oxidation, first, an aldehyde containing the group $(\text{CHO})'$ and then an acid containing the group $(\text{COOH})'$, both aldehyde and acid containing the same number of carbon atoms as the alcohol. These alcohols contain the characterizing group $(\text{CH}_2\text{OH})'$, and are called **primary alcohols**, *e.g.*, ethylic alcohol: $\text{CH}_3.\text{CH}_2\text{OH}$.

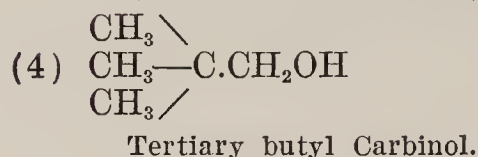
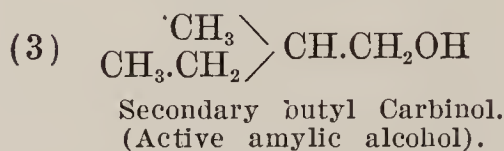
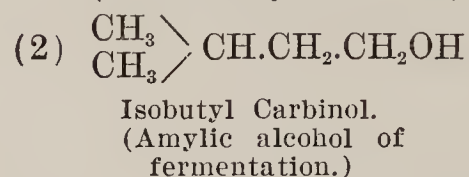
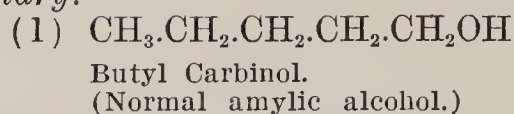
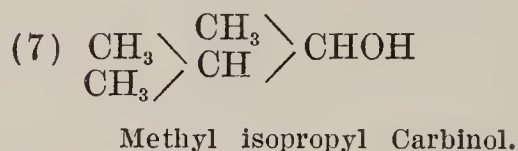
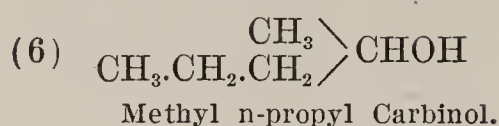
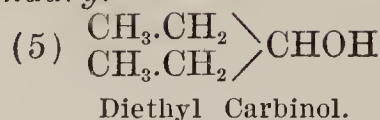
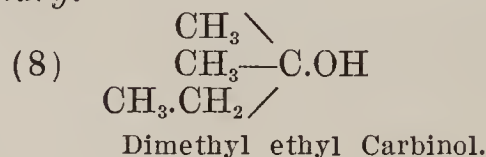
II. Other monoatomic alcohols yield on oxidation not an aldehyde or an acid, but a ketone, containing the group $(\text{CO})''$ and the same number of carbon atoms as the alcohol. These alcohols contain the characterizing group $(\text{CHOH})''$, and are called **secondary alcohols**, or **isوالcohols**, *e.g.*, Isopropyl alcohol: $\text{CH}_3.\text{CHOH}.\text{CH}_3$.

III. Still other alcohols yield on oxidation either two or more acids, or an acid and a ketone, whose molecules contain a less number of carbon atoms than the alcohol from which they were derived. These alcohols contain the characterizing group $(\text{COH})'''$, and are called **tertiary alcohols**, *e.g.*, Tertiary butyl alcohol, $(\text{CH}_3)_3:\text{COH}$.

The monohydric alcohols are also the hydroxides of the *alkyls* (p. 202).

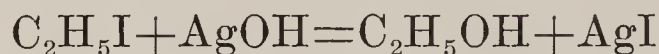
Nomenclature.—Names of alcohols terminate in *ol*; and the termination *ol* is reserved for the names of alcohols and of phenols. The "Geneva" names of the monohydric alcohols are derived from those of the corresponding hydrocarbons by the substitution of the syllable *ol* for the terminal *e*: Thus $\text{H}.\text{CH}_2\text{OH}$ is methanol; $\text{CH}_3.\text{CH}_2\text{OH}$ ethanol; $\text{CH}_3.\text{CH}_2\text{CH}_2\text{OH}$, 1-propanol; $\text{CH}_3.\text{CHOH}.\text{CH}_3$, 2-propanol, etc.

Kolbe's system of naming the monoatomic alcohols is more generally followed. It refers the names of the higher alcohols back to that of the first, $\text{H}.\text{CH}_2\text{OH}$, which is called **carbinol**; the names of the radicals contained in the superior homologues being prefixed to the word "*carbinol*" in the construction of their names. Thus the graphic formulæ and **carbinol names** of the eight possible amyllic alcohols are as follows:

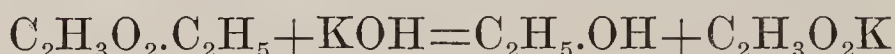
Primary.*Secondary.**Tertiary.*

Of the above, numbers 1, 5 and 6 are derived from the normal paraffin (1, p. 202); numbers 2, 3, 7 and 8 from the isoparaffin (2), and number 4 from the mesoparaffin (3).

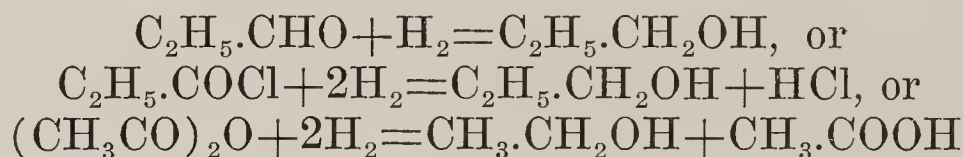
General Methods of Formation.—(1) By the action of freshly precipitated, moist silver hydroxide upon the haloid esters:



(2) By the saponification of their esters by caustic potash:



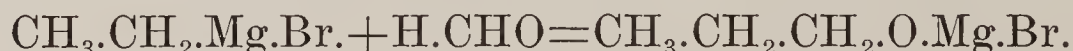
(3) Primary alcohols are produced by the reduction of aldehydes, acid chlorides, or anhydrides:



(4) By the action of nitrous acid upon the primary amines:



(5) By the action of trioxymethylene upon the alkyl magnesium halides (p. 291); the alcohol next above the alkyl contained in the organo-metallic compound being formed. This reaction, after the trioxymethylene splits to formic aldehyde (p. 228), takes place in two stages. A condensation product is first formed:

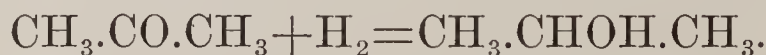


And this is then hydrolyzed:



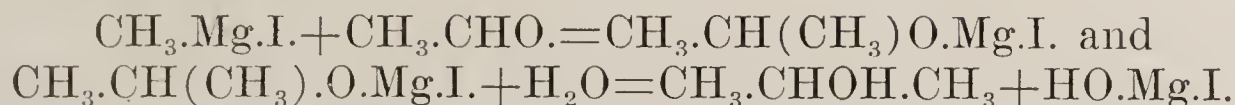
(p. 291).

(6) Secondary alcohols are formed by the reduction of ketones:

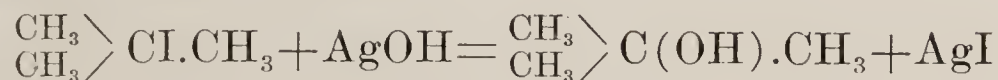


(7) With aldehydes higher than formic aldehyde, alkyl mag-

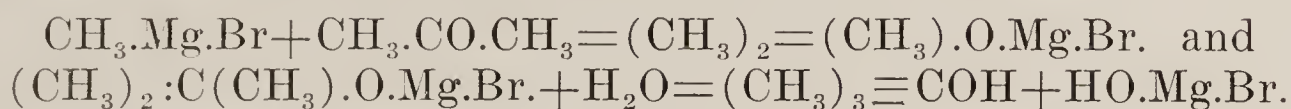
nesium halides produce secondary alcohols, the reactions occurring in two phases as in (5) :



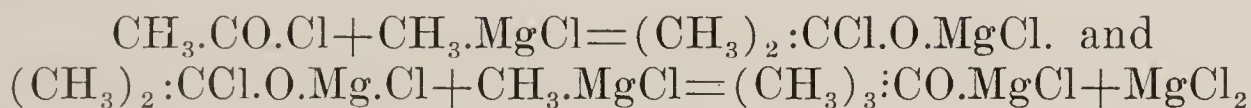
(8) Tertiary alcohols are produced by the action of moist silver hydroxide upon tertiary alkyl iodides. Thus tertiary butyl iodide yields tertiary butyl alcohol:



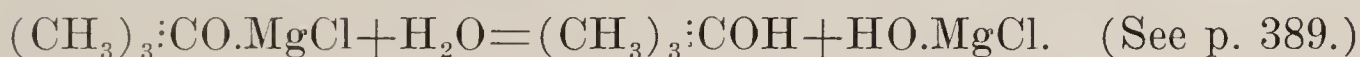
(9) With ketones the alkyl magnesium halides produce tertiary alcohol by reactions similar to those given (in 5 and 7) :



(10) Acetyl chloride or anhydride reacts violently with alkyl magnesium halides. At suitable temperature this reaction occurs in two stages :

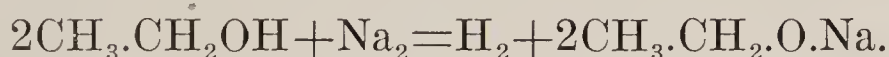


The product when hydrolyzed yields a tertiary alcohol :

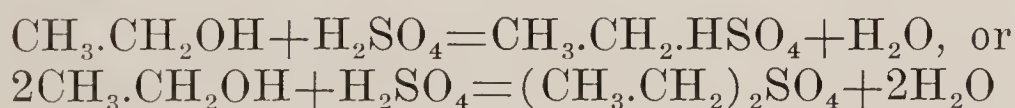


(11) Tertiary alcohols are also produced by interaction of alkyl magnesium halides with esters of monobasic acids (except formic), or with carbonyl chloride. Formic esters yield secondary alcohols (p. 290).

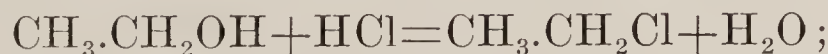
General Reactions.—(1) The monohydric alcohols react with metallic Na or K to form double oxides, called **alcoholates** :



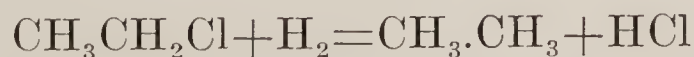
(2) When heated with acids they form esters :



(3) When heated with hydracids they form alkyl halides :

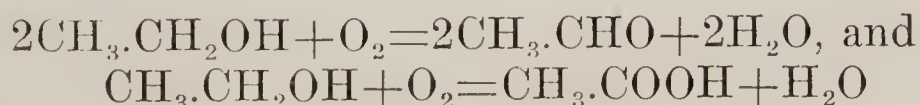


which, in turn, when reduced by nascent hydrogen, regenerate the parent hydrocarbon :

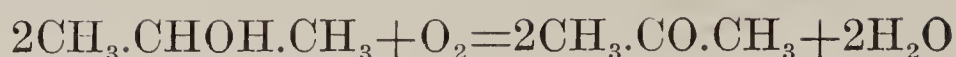


(4) Their products of oxidation vary according as they are primary, secondary or tertiary (see above) :

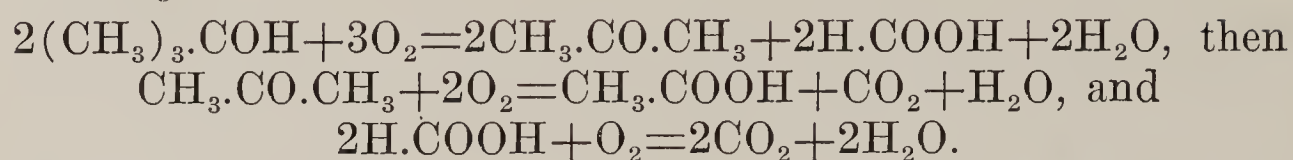
Primary:



Secondary:



Tertiary:



Methyl Hydroxide—Carbinol—Pyroxylic spirit—Methylic alcohol—Wood alcohol—Wood spirit— $\text{H}.\text{CH}_2\text{OH}=32$ —may be formed from marsh-gas, CH_4 , by first converting it into the iodide, and acting upon this with potassium hydroxide:



It is usually obtained by the destructive distillation of wood. The pure hydroxide can only be obtained by decomposing a crystalline compound, such as methyl oxalate, and rectifying the product until the boiling-point is constant at 66.5° .

Pure methyl alcohol is a colorless liquid, having an ethereal and alcoholic odor, and a sharp, burning taste; sp. gr. 0.814 at 0° ; boils at 66.5° ; burns with a pale flame, giving less heat than that of ethylic alcohol; mixes with water, alcohol, and ether in all proportions; is a good solvent of resinous substances, and also dissolves sulphur, phosphorus, potash, and soda.

Methyl hydroxide is not affected by exposure to air under ordinary circumstances, but in the presence of platinum-black it is oxidized, with formation of the corresponding aldehyde, formaldehyde, and acid, formic acid. Hot HNO_3 decomposes it with formation of nitrous fumes, formic acid and methyl nitrate. It is acted upon by H_2SO_4 in the same way as ethyl alcohol. The organic acids form methyl esters with it.

Methylated spirit is ethyl alcohol containing one-ninth its volume of wood spirit.

Ethyl Hydroxide—Ethylic alcohol—Methyl carbinol—Vinic alcohol—Alcohol—Spirits of wine— $\text{CH}_3.\text{CH}_2\text{OH}=46$.

Preparation.—Industrially alcohol and alcoholic liquids are obtained from substances rich in starch or glucose.

The manufacture of alcohol consists of three distinct processes: (1) the conversion of starch into sugar; (2) the fermentation of the saccharine liquid; (3) the separation, by distillation, of the alcohol formed by fermentation.

(1) The raw materials for the first process are **malt** and some substance (grain, potatoes, rice, corn, etc.) containing starch. Malt is barley which has been allowed to germinate, and, at the proper stage of germination, roasted. During this growth there is developed in the barley a peculiar nitrogenous principle called **diastase**. The starchy material is mixed with a suitable quantity of malt and water,

and the mass maintained at a temperature of 65° – 70° for two to three hours, during which the diastase rapidly converts the starch into **dextrin**, and this in turn into **maltose** and **glucose**.

(2) The saccharine fluid, or **wort**, obtained in the first process, is drawn off, cooled, and **yeast** is added. As a result of the growth of the yeast-plant, a complicated series of chemical changes takes place, the principal one of which is the splitting up of the glucose into carbon dioxide and alcohol:



There are formed at the same time small quantities of glycerol, succinic acid, and propylic, butylic, and amylic alcohols.

(3) An aqueous fluid is thus obtained which contains 3–15 per cent. of alcohol. This is then separated by the third process, that of distillation and rectification. The apparatus used for this purpose has been so far perfected that by a single distillation an alcohol of 90–95 per cent. can be obtained.

In some cases alcohol is prepared from fluids rich in glucose, such as grape-juice, molasses, syrup, etc. In such cases the first process becomes unnecessary.

Commercial alcohol always contains H_2O , and when pure or *absolute* alcohol is required, the commercial product must be mixed with some hygroscopic solid substance, such as quicklime, from which it is distilled after having remained in contact twenty-four hours.

Fermentation.—This term (derived from *fervere*=to boil) was originally applied to alcoholic fermentation, by reason of the bubbling of the saccharine liquid caused by the escape of CO_2 ; subsequently it came to be applied to all decompositions similarly attended by the escape of gas.

At present it is used by many authors to apply to a number of heterogeneous processes; and some writers distinguish between “true” and “false” fermentation. It is best to limit the application of the term to those decompositions designated as *true fermentations*.

Fermentation is a decomposition of an organic substance, produced by the processes of nutrition of a low form of animal or vegetable life.

The **true ferments** are therefore all organized beings, such as *torula cerevisiæ*, producing alcoholic fermentation; *penicillium glaucum*, producing lactic acid fermentation; and *mycoderma aceti*, producing acetic acid fermentation.

Acetic acid fermentation. The micro-organism, which is present in the air, causes the alcohol to take up oxygen from the air; acetic acid is produced:



Lactic acid fermentation. The micro-organism, which is present in the air, gets into the milk and converts the lactose into lactic acid:

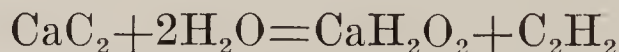


Butyric acid fermentation. This is brought about when decaying cheese and sour milk are brought together; the lactic acid is converted into butyric acid by the butyric ferment which is present in the cheese:

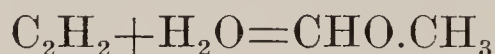


The **false fermentations** are not produced by an organized body, but by a soluble, unorganized, nitrogenous substance, whose method of action is as yet imperfectly understood. The unorganized ferments, such as diastase, pepsin, etc., are called **enzymes**.

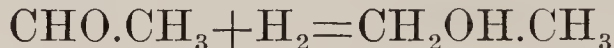
An interesting total synthesis of alcohol is from calcium carbide, water and hydrogen. Acetylene is formed by the action of water upon calcium carbide:



Vapors of acetylene and water, heated together to 325° unite to form aldehyde:

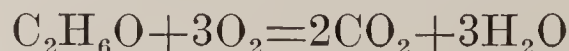


And nascent hydrogen converts aldehyde into alcohol:



Properties.—Alcohol is a thin, colorless, transparent liquid, having a spirituous odor and a sharp, burning taste; sp. gr. 0.8095 at 0° , 0.7939 at 15° ; it boils at 78.5° , and solidifies at -130.5° . At temperatures below -90° it is viscous. It mixes with water in all proportions, the union being attended by elevation in temperature and contraction in volume (after cooling to the original temperature). It also attracts moisture from the air to such a degree that absolute alcohol only remains such for a very short time after its preparation. It is to this power of attracting H_2O that alcohol owes its preservative power for animal substances. It is a very useful solvent, dissolving a number of gases, many mineral and organic acids and alkalies, most of the chlorides and carbonates, some of the nitrates, and the essences and resins. The sulphates are insoluble in alcohol. Alcoholic solutions of fixed medicinal substances are called **tinctures**; those of volatile principles, **spirits**.

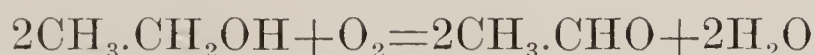
The action of oxygen upon alcohol varies according to the conditions. Under the influence of energetic oxidants, such as chromic acid, or, when alcohol is burned in the air, the oxidation is rapid and complete, and is attended by the extrication of much heat, and the formation of carbon dioxide and water:



Mixtures of air and vapor of alcohol explode upon contact with flame. If a less active oxidant be used, such as platinum-black, or by the action of atmospheric oxygen at low temperatures, a simple oxidation of the alcoholic radical takes place, with formation of *acetic acid*:



a reaction which is utilized in the manufacture of acetic acid and vinegar. If the oxidation is still further limited, *aldehyde* is formed:



If vapor of alcohol is passed through a tube filled with platinum sponge and heated to redness, or if a coil of heated platinum wire is introduced into an atmosphere of alcohol vapor, the products of oxidation are quite numerous: among them are water, ethylene, aldehyde, acetylene, carbon monoxide, and acetal. Heated platinum wire introduced into vapor of alcohol continues to glow by the heat resulting from the oxidation, a fact which has been utilized in the thermocautery.

Chlorine and bromine act energetically upon alcohol, producing a number of chlorinated and brominated derivatives, the final products being *chloral* and *bromal*. If the action of Cl is moderated, aldehyde and HCl are first produced. Iodine acts quite slowly in the cold but old solutions of I in alcohol (Tr. iodine) are found to contain HI, ethyl iodide, and other imperfectly studied products. In the presence of an alkali, I acts upon alcohol to produce iodoform, which is also formed under like conditions from aldehyde or acetone. Potassium and sodium dissolve in alcohol with evolution of H; upon cooling, a white solid crystallizes, which is the double oxide of ethyl and the alkali metal, and is known as potassium or sodium **ethylate** or **alcoholate**. Nitric acid, aided by a gentle heat, acts violently upon alcohol, producing nitrous ether, brown fumes, and products of oxidation. (For the action of other acids upon alcohol see the corresponding esters and the ethers.) The hydroxides of the alkali metals dissolve in alcohol, but react upon it slowly; the solution turns brown and contains an acetate. If alcohol is gently heated with HNO₃ and nitrate of silver or of mercury, a gray precipitate falls, which is silver or mercury fulminate.

Varieties.—It occurs in different degrees of concentration: **absolute alcohol** is pure alcohol, C₂H₆O. It is not purchasable, and must be made as required. **Alcohol dehydratum** (U. S. P.) contains not less than 99 per cent. by weight of C₂H₅OH. The so-called absolute alcohol of the shops is rarely stronger than 98 per cent. **Alcohol** (U. S. P.), sp. gr. 0.820, contains 94 per cent. by volume, and **spiritus rectificatus**, sp. gr. 0.838, contains 84 per cent. This is the ordinary rectified spirit used in the arts. **Alcohol dilutum** (U. S. P.)

used in the preparation of tinctures, contains 41 per cent. It is of about the same strength as the **proof spirit** of commerce. **Denatured alcohol** is alcohol which, while fit for industrial uses, has been rendered unfit for drinking. This is accomplished by the addition of substances, such as methyl alcohol and pyridine or benzine.

Analytical Characters.—(1) Heated with a small quantity of solution of potassium dichromate and H_2SO_4 , the liquid assumes an emerald-green color, and, if the quantity of $\text{C}_2\text{H}_6\text{O}$ is not very small, the peculiar fruity odor of aldehyde is developed. (2) Warmed and treated with a few drops of potash solution and a small quantity of iodine, an alcoholic liquid deposits a yellow, crystalline ppt. of iodoform, either immediately or after a time. (3) If HNO_3 is added to a liquid containing $\text{C}_2\text{H}_6\text{O}$, nitrous ether, recognizable by its odor, is given off. If a solution of mercurous nitrate with excess of HNO_3 is then added, and the mixture heated, a further evolution of nitrous ether occurs, and a yellow-gray deposit of fulminating mercury is formed, which may be collected, washed, dried, and exploded. (4) If an alcoholic liquid is heated for a few moments with H_2SO_4 diluted with H_2O and distilled, the distillate, on treatment with H_2SO_4 and potassium permanganate, and afterward with sodium thiosulphate, yields aldehyde, which may be recognized by the production of a violet color with a dilute solution of fuchsin.

None of the above reactions, *taken singly*, is characteristic of alcohol.

Alcohol is determined quantitatively in simple mixtures of alcohol and water by determining the specific gravity and referring to tables constructed for the purpose. In alcoholic beverages 100 cc. of the sample is distilled until 75 cc. have passed over; the distillate is then made up to 100 cc. with water, and the sp. gr. determined.

Alcoholic Beverages.—These may be divided into four classes:

I.—Those prepared by the fermentation of malted grain—**beers, ales and porters**.

II.—Those prepared by the fermentation of grape juice—**wines**.

III.—Those prepared by the fermentation of the juices of fruits other than the grape—**cider, fruit-wines**.

IV.—Those prepared by the distillation of some fermented saccharine liquid—**ardent spirits**.

Beer, ale and porter are aqueous infusions or decoctions of malted grain, fermented and flavored with hops. They contain all of the soluble constituents of the grain and hops, plus dextrins, maltose, glucose, alcohol and carbon dioxide. Their alcoholic contents varies from 1.5 to 9 per cent. absolute alcohol by weight. They contain a considerable proportion of nitrogenous material (0.4 to 1 per cent. N), and succinic, lactic and acetic acids. The most serious *adulterations* of malt liquors consist in the use of artificial glucose to furnish a part of the alcohol, and in the use of strychnine, picrotoxin, picric acid, or other bitter principles as substitutes for hops.

Wine is fermented grape-juice. The expressed juice, called the **must**, contains much glucose, the fermentation of which is set up by yeast-plants growing upon the grape-skins. In *red* wines the color is produced by solution of the

coloring matter of the skins in the accumulating alcohol. The same agency causes the precipitation of a part of the hydropotassic tartrate, to which the grape or wine owes its tartness. *Sweet* wines are made from grapes rich in glucose, and by arresting the fermentation before the sugar has been completely decomposed. "*Dry*" or "*brut*" wines, which are not sweet, are fermented to completion. "*Light*" wines are such as contain less than 12 per cent. of alcohol, although they sometimes contain as much as 16 per cent. They are the products of temperate climates, and include the elarets, Sauternes, Burgundies, the Rhine, Moselle, Australian, Greek and Hungarian wines, and the wines of the northern portions of Spain, Italy and the United States. The champagnes also belong to this class, and are sparkling from the escape of carbon dioxide, produced by a secondary fermentation in the bottles, and held in solution by its own pressure. "*Heavy*" wines are those whose alcoholic strength is greater than 12 per cent., usually 14 to 25 per cent. They are the products of warm climates, and include the sherries of the south of Spain, the ports of Portugal, the Marsalas of the south of Italy, the Madeiras, and the wines of southern California. The *adulteration* of real wine is practically limited to the addition of coloring matters, and to "fortification" by the addition of alcohol or brandy. Liquids are also manufactured to imitate wines, which contain no grape-juice.

Cider is the fermented juice of the apple, and contains from 3.5 to 7.5 per cent. of alcohol.

Spirits are prepared by fermentation and distillation. They differ from beers and wines in containing a larger percentage of alcohol, 35 to 50 per cent., and in not containing any of the non-volatile constituents of the grains or fruits from which they are prepared. They are yellow in color when stored in white oak casks the interior of which has been burnt, and colorless or faintly yellow when kept in unburnt casks. Besides alcohol and water they contain acetic, butyric, valeric and cænanthic esters, to which they owe their flavor. They include: *brandy*, sp. gr. 0.929–0.934, made by distilling wine; *rum*, sp. gr. 0.914–0.926, made by distilling molasses; and *whiskies* and *gins*, made by fermenting and distilling grains, wheat, rye, barley or maize. The peculiar flavor of *Scotch* and *Irish whiskies* is derived from the smoke of a peat fire; that of *gin* is produced by distilling from juniper berries. In making *straight whisky* the distillate is not completely defuselated (p. 220), and by slow oxidation the remaining fusel produces the esters to which the spirit owes its flavor. Hence when newly made it is neither palatable nor wholesome, but in about three years in wood the fusel has been in great part removed by oxidation, the whisky is *ripe*, and continues to improve with age. In making *blend whisky* the distillate is completely defuselated to *neutral spirit*, and the product is made to imitate aged whisky more or less closely by addition of esters, "beading oil" and other chemicals.

Liqueurs or **cordials** are spirits sweetened and flavored with vegetable aromatics, and frequently colored; *anissette* is flavored with aniseed; *absinthe*, with wormwood; *curaçoa*, with orange peel; *kirschwasser*, with cherries, the stones being cracked and the spirits distilled from the bruised fermented fruit; *kümmel*, with cummin and caraway seeds; *maraschino*, with cherries; *noyau*, with peach and apricot kernels.

Propyl Hydroxide—**Ethyl carbinol**—**Primary propyl alcohol**— $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ —60—is produced, along with ethylic alcohol, during fermentation, and obtained by fractional distillation of marc brandy, from *cognac oil*, *huile de marc* (not to be confounded with oil of wine), an oily matter, possessing the flavor of inferior brandy, which separates from marc brandy, distilled at high temperatures; and from the residues of manufacture of alcohol from beet-root, grain, molasses, etc. It is a colorless liquid, has a hot alcoholic taste, and a fruity odor; boils at 96.7° ; and is miscible with water. It has not been put

to any use in the arts. Its intoxicating and poisonous actions are greater than those of ethyl alcohol. It exists in small quantity in cider.

Butyl Alcohols— C_4H_9OH —74.—The four butyl alcohols theoretically possible are known to exist:

Propyl Carbinol—**Primary normal butyl alcohol**—*Butyl alcohol of fermentation*— $CH_3.CH_2.CH_2.CH_2OH$ —is formed in small quantities during alcoholic fermentation, and may be obtained by repeated fractional distillation from the oily liquid left in the rectification of vinic alcohol. It is a colorless liquid; boils at 116.8° . It is more actively poisonous than ethyl or methyl alcohol.

Isopropyl Carbinol—**Isobutyl alcohol**— $\begin{matrix} CH_3 \\ \diagdown \\ CH \\ \diagup \\ CH_3 \end{matrix} .CH_2.OH$ —occurs in the fusel oil obtained in the products of fermentation and distillation of beet-root molasses. It is a colorless liquid, sp. gr. 0.8032; boils at 108.4° .

Ethyl-methyl Carbinol—**Secondary butyl alcohol**— $CH_3-CH_2-\begin{matrix} \diagdown \\ CH \\ \diagup \\ CH_3 \end{matrix} .CHOH$ —a liquid which boils at 99° .

Trimethyl Carbinol—**Tertiary butyl alcohol**, $\begin{matrix} CH_3 \\ \diagdown \\ CH_3-C-OH \\ \diagup \\ CH_3 \end{matrix}$ —a crystalline solid which fuses at 25° , and boils at 82° .

Amylic Alcohols— $C_5H_{11}OH$ —88.—The eight amyl alcohols theoretically possible (see p. 212) are known. The substance usually known as **amylic alcohol**, **potato spirit**, **fusel oil**, is the primary alcohol, $\begin{matrix} CH_3 \\ \diagdown \\ CH \\ \diagup \\ CH_3 \end{matrix} .CH_2.CH_2.OH$, with lesser quantities of other alcohols, differing in nature and amount with the grain used, and the conditions of the fermentation and distillation, each kind of "spirit" furnishing and containing a peculiar fusel.

In the process of manufacture of ardent spirits the fusel oil accumulates in great part in the still, but much of it distils over, and is more or less completely removed from the product by the process of **defuselation**.

The individual amylic alcohols have the following characters:

Butyl carbinol; **normal amylic alcohol**,— $CH_3.CH_2.CH_2.CH_2.CH_2OH$ —is a colorless liquid, boils at 137° . Obtained from normal butyl alcohol, or from normal amylamine. It yields normal valeric acid on oxidation.

Isobutyl Carbinol—**Amyl alcohol**— $\begin{matrix} CH_3 \\ \diagdown \\ CH \\ \diagup \\ CH_3 \end{matrix} .CH_2.CH_2.OH$ —is the principal constituent of the fusel oil from grain and potatoes. It is obtained from the last milky products of rectification of alcoholic liquids. These are shaken with H_2O to remove ethyl alcohol, the supernatant oily fluid is decanted, dried by contact with fused calcium chloride, and distilled; that portion which passes over between 128° and 132° being collected.

It is a colorless, oily liquid, has an acrid taste and a peculiar odor, at first not unpleasant, afterward nauseating and provocative of severe headache. It boils at 131.4° , and crystallizes at -20° ; sp. gr. 0.8184 at 15° . It mixes with alcohol and ether, but not with water. It burns with a pale blue flame when sufficiently heated.

When exposed to air it oxidizes very slowly; quite rapidly, however, in contact with platinum-black, forming isovaleric acid. The same acid, along with other substances, is produced by the action of the more powerful oxidants upon amyl alcohol. Chlorine attacks it energetically, forming amyl chloride, $C_5H_{11}Cl$, and other chlorinated derivatives. Sulphuric acid dissolves in amyl

alcohol, with formation of amyl-sulphuric acid, $\text{SO}_4(\text{C}_5\text{H}_{11})\text{H}$, corresponding to ethyl-sulphuric acid (p. 277). It also forms similar acids with phosphoric, oxalic, citric, and tartaric acids. Its esters, when dissolved in ethyl alcohol, have the taste and odor of various fruits, and are used in the preparation of artificial fruit-essences. Amyl alcohol is also used in analysis as a solvent, particularly for certain alkaloids, and in pharmacy for the artificial production of valeric acid and the valerates.

Diethyl Carbinol— $\begin{array}{c} \text{CH}_3-\text{CH}_2 \\ \text{CH}_3-\text{CH}_2 \end{array} \rangle \text{CHOH}$ —is produced by the action of a mixture of zinc and ethyl iodide on ethyl formate, with the subsequent addition of H_2O . It is a liquid which boils at 116.5° .

Methyl-propyl Carbinol— $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3-\text{CH}_2-\text{CH}_2 \end{array} \rangle \text{CHOH}$ —a liquid, boiling at 118.5° , obtained by the hydrogenation of methyl-propylic acetone.

Methyl-isopropyl Carbinol— $\begin{array}{c} \text{CH}_3 \\ (\text{CH}_3)_2=\text{CH} \end{array} \rangle \text{CHOH}$ —obtained by the hydrogenation of methyl-isopropylic acetone; or by the action of hydriodic acid upon amylene, and the action of moist silver oxide upon the product so obtained. It is a colorless liquid, sp. gr. 0.829 at 0° , having a pungent, ethereal odor; boils at 112.5° , soluble in H_2O and in alcohol.

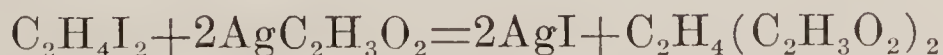
Ethyl-dimethyl Carbinol—*Tertiary amylic alcohol*—*Amylene hydrate*— $\begin{array}{c} \text{CH}_3 \backslash \\ \text{CH}_3-\text{CH}_2-\text{COH} \\ \text{CH}_3 / \end{array}$ —is a liquid which solidifies at -12° , and boils at 102.5° ; formed by the action of zinc methyl upon propionyl chloride, or by decomposition of tertiary sulphamylic acid by boiling H_2O . The nitrite of this alcohol has been used as a substitute for amyl nitrite.

DIATOMIC, OR DIHYDRIC ALCOHOLS; GLYCOLS.

The paraffin glycols are derived from the paraffins by the substitution of two hydroxyls for two H atoms. They bear the same relation to the monoatomic alcohols that the diacid bases bear to the monacid bases. They are diprimary, disecundary, primary-secondary, etc., according as they contain groups CH_2OH ; CHOH , or COH . Their “Geneva” names are derived from those of the parent hydrocarbons by the substitution of the syllable “*diol*” for the terminal *e*; and they are distinguished as α , β , γ , δ , etc., according as the hydroxyls occupy 1:2, 1:3, 1:4, 1:5, etc., positions. Thus the primary-secondary glycol $\text{CH}_2\text{OH}.\text{CH}_2.\text{CHOH}.\text{CH}_3$, is β -butandiol.

As the monohydric alcohols are regarded as the hydroxides of the univalent *alkyls*, so the dihydric alcohols are considered as the hydroxides of bivalent hydrocarbon radicals: $(\text{C}_2\text{H}_4)'' : (\text{OH})_2$, which are called **alkylenes**.

They may be obtained from the neutral haloid esters by heating with silver acetate:

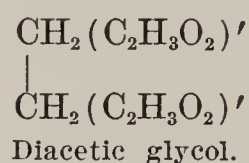
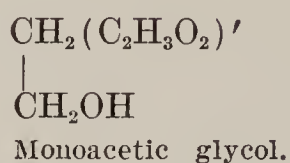
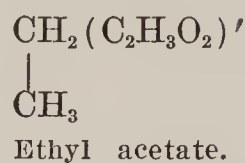


And saponification of the ester so formed by caustic potash:



While the monoatomic alcohols are only capable of forming a sin-

gle ester with a monobasic acid, the glycols are capable of forming two such esters:



Ethene Glycol—Ethylene glycol, or alcohol, or hydroxide— $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ —62.—This, the best known of the glycols, is prepared by the action of dry silver acetate upon ethylene bromide. The ester so obtained is purified by redistillation, and decomposed by heating for some time with barium hydroxide.

It is a colorless, slightly viscous liquid; odorless; faintly sweet; sp. gr. 1.125 at 0°; boils at 197°; sparingly soluble in ether; very soluble in water and in alcohol.

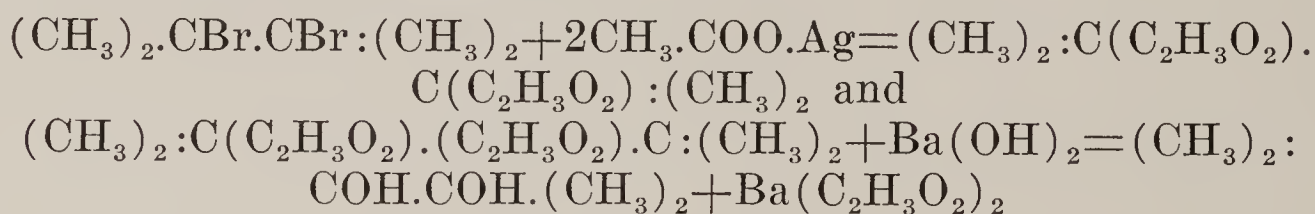
It is not oxidized by simple exposure to air, but on contact with platinum-black it is oxidized to glycolic acid; more energetic oxidants transform it into oxalic acid. Chlorine acts slowly upon glycol in the cold; more rapidly under the influence of heat, producing chlorinated and other derivatives. By the action of dry HCl upon cooled glycol, a product is formed, intermediate between it and ethylene chloride, a neutral compound—**ethene chlorhydrine**, $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{Cl} \end{array}$, which boils at 130°.

Ditertiary glycols are produced by the action of organic magnesium halides upon the esters of dibasic acids in the same manner as tertiary monohydric alcohols are formed from those of monobasic acids (p. 213).

Pinacone or **tetramethylethylene glycol** is a ditertiary alcohol produced by the action of nascent hydrogen (sodium) upon acetone:



It is also formed by the successive action of silver acetate and barium hydroxide on hexylene dibromide:

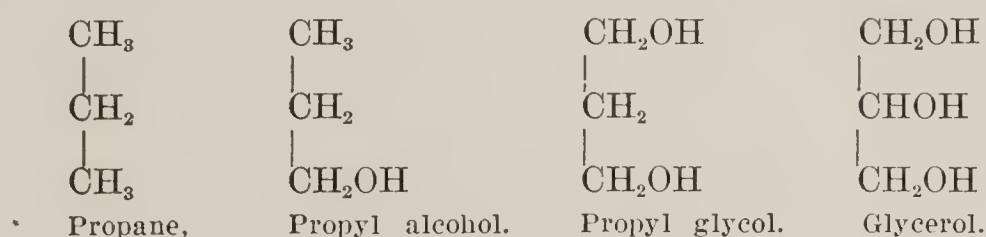


It is also produced by the general method, by the action of magnesium methiodide upon ethyl oxalate.

TRIATOMIC, OR TRIHYDRIC ALCOHOLS; GLYCEROLS.

These are derived from the paraffins by the substitution of three hydroxyls for three hydrogen atoms, linked to different carbon atoms. The simplest triprimary glycerol, which would have the formula:

$\text{CH}(\text{CH}_2\text{OH})_3$, is unknown. The simplest known representative of the class is the ordinary glycerine, more properly called **glycerol**, which is diprimary-secondary. The relations of the monoatomic, diatomic, and triatomic alcohols to each other and to the parent hydrocarbon are shown in the following formulæ:



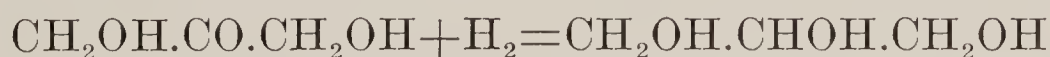
The Geneva names of the glycerols are derived from those of the hydrocarbons by the substitution of the syllable “*triol*” for the terminal *e*. Thus glycerol is **propantriol**.

They are obtained by the saponification of their esters, either those existing in nature or those produced artificially.

They combine with acids to form three series of esters, known generically as **monoglycerides**, **diglycerides**, and **triglycerides**, formed by the combination of one molecule of the alcohol with one, two, or three molecules of a monobasic acid. The names of the individual esters terminate in *in*, and have a prefix indicating the number of acid residues. Thus: $\text{C}_3\text{H}_5(\text{OH})_2 \cdot \text{C}_2\text{H}_3\text{O}_2$ is **monacetin**, $\text{C}_3\text{H}_5(\text{OH}) (\text{C}_2\text{H}_3\text{O}_2)_2$ is **diacetin**, and $\text{C}_3\text{H}_5(\text{C}_2\text{H}_3\text{O}_2)_3$ is **triacetin**.

Glycerol—Glycerine—Propenyl alcohol—Glycerinum (U. S. P.)— $\text{C}_3\text{H}_5(\text{OH})_3$ —92—was first obtained as a secondary product in the manufacture of lead plaster; it is now produced as a by-product in the manufacture of soaps and of stearin candles. It exists free in palm-oil and in other vegetable oils. It is produced in small quantity during alcoholic fermentation, and is consequently present in wine and beer. It is much more widely disseminated in its esters, the neutral fats, in the animal and vegetable kingdoms.

It has been obtained by partial synthesis, by heating a mixture of allyl tribromide, silver acetate and acetic acid, and saponifying the triacetin so obtained. Also by total synthesis, by reduction of dioxyacetone by sodium amalgam in presence of aluminium sulphate:



Glycerol obtained by saponification of fats, and purified by distillation in a current of superheated steam, known as “distilled glycerine,” is reasonably pure. The only impurities likely to be present are water, and sometimes arsenic.

Glycerol is a colorless, odorless, syrupy liquid, has a sweetish taste; sp. gr. 1.26 at 15° . Although it cannot usually be caused to crystallize by the application of the most intense cold, it does so sometimes under imperfectly understood conditions, forming small, white needles of sp. gr. 1.268, and fusible between 17° and 18° .

It is soluble in all proportions in water and alcohol, insoluble in ether and in chloroform. It is a good solvent for a number of mineral and organic substances (*glycerites* and *glyceroles*). It is not volatile at ordinary temperatures. When impure glycerol is heated, a portion distils unaltered at 275° – 280° , but the greater part is decomposed into acrolein, acetic acid, carbon dioxide, and combustible gases. It may be distilled unchanged in a current of superheated steam between 285° and 315° . Pure glycerol distils unchanged at 290° at a pressure of 756 mm., and at 180° at 20 mm.

Concentrated glycerol, when heated to 150° ignites and burns without odor and without leaving a residue, and with a pale blue flame. It may also be burnt from a short wick.

Glycerol is readily oxidized, yielding different products with different degrees of oxidation. Platinum-black oxidizes it, with formation, finally, of H_2O and CO_2 . Oxidized by manganese dioxide and H_2SO_4 , it yields CO_2 and formic acid. If a layer of glycerol diluted with an equal volume of H_2O is floated on the surface of HNO_3 of sp. gr. 1.5, a mixture of several acids is formed: oxalic, $\text{C}_2\text{H}_2\text{O}_4$; glyceric, $\text{C}_3\text{H}_6\text{O}_4$, formic, CH_2O_2 ; glycollic, $\text{C}_2\text{H}_4\text{O}_3$; glyoxylic, $\text{C}_2\text{H}_4\text{O}_4$; and tartaric, $\text{C}_4\text{H}_6\text{O}_6$. When glycerol is heated with potassium hydroxide, a mixture of potassium acetate and formate is produced. When glycerol, diluted with 20 volumes of H_2O , is heated with Br ; CO_2 , bromoform, glyceric acid, and HBr are produced. Phosphoric anhydride removes the elements of H_2O from glycerol, with formation of acrolein (p. 330). A similar action is effected by heating with H_2SO_4 , or with monopotassic sulphate. Heated with oxalic acid, glycerol yields CO_2 and formic acid.

The presence of glycerol in a liquid may be detected as follows: Add NaOH to feebly alkaline reaction, and dip into it a loop of Pt wire holding a borax bead; then heat the bead in the blow-pipe flame, which is colored green if the liquid contain $\frac{1}{100}$ of glycerol.

The glycerol used for medicinal purposes should respond to the following tests: (1) its sp. gr. should not vary much from that given above; (2) it should not rotate polarized light; (3) it should not turn brown when heated with sodium nitrate; (4) it should not be colored by H_2S ; (5) when dissolved in its own weight of alcohol, containing one per cent. of H_2SO_4 , the solution should be clear; (6) when mixed with an equal volume H_2SO_4 , of sp. gr. 1.83, it should form a limpid, brownish mixture, but should not give off gas.

POLYATOMIC, OR POLYHYDRIC ALCOHOLS.

Tetratomic Alcohols contain four hydroxyls. The best known is:

Erythrol—*Erythrite*— $\text{CH}_2\text{OH}(\text{CHOH})_2\text{CH}_2\text{OH}$ —which is a product of decomposition of **erythrin**, $\text{C}_{20}\text{H}_{22}\text{O}_{10}$, which exists in the lichens of the genus *rocella*. It crystallizes in large, brilliant prisms; very soluble in H_2O and in hot alcohol, almost insoluble in ether; sweetish in taste; its solutions neither

affect polarized light, nor reduce Fehling's solution, nor are capable of fermentation. Its watery solution, like that of sugar, is capable of dissolving a considerable quantity of lime, and from this solution alcohol precipitates a definite compound of erythrite and calcium. By oxidation with platinum-black it yields **erythroglucic acid**, $C_4H_8O_5$. With fuming HNO_3 it forms a tetranitro compound, which explodes under the hammer.

Pentatomic, or Pentahydric Alcohols—Pentites—contain five hydroxyls. The only member of the group known to exist in nature is the simplest $C_5H_7(OH)_5$, called **adonite**, obtained from *Adonis vernalis*. Other members of the series are obtained by reduction of the corresponding aldopentoses.

Hexatomic, or Hexahydric Alcohols—Hexites—contain six hydroxyls. They are closely related to the sugars, which they resemble in their properties, although they do not reduce Fehling's solution, and are not fermented by yeast. They are obtained by reduction of the corresponding glucoses, aldohexoses and ketohexoses. Three hexites occur in nature:

Mannitol—Mannite— $CH_2OH.(CHOH)_4.CH_2OH$ —constitutes the greater part of manna, and also exists in a number of other plants. It is also produced during the so-called mucic fermentation of sugar, and during lactic fermentation. It crystallizes in long prisms, odorless, sweet; fuses at 166° and crystallizes on cooling; boils at 200° , at which temperature it is converted into **mannitan**, $C_6H_{12}O_5$; soluble in H_2O , very sparingly in alcohol.

Sorbitol—Sorbite—occurs in mountain-ash berries. It forms crystals, soluble in water.

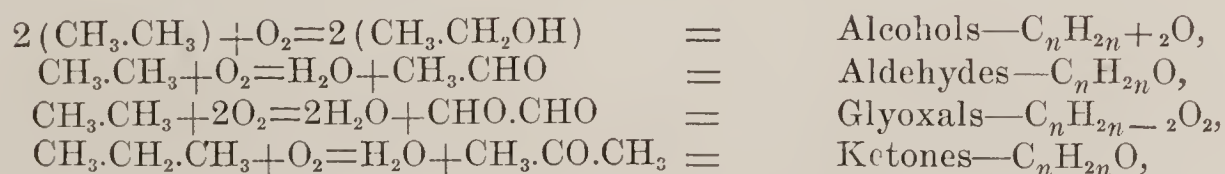
Dulcitol—Dulcite—Melampyrite—Dulcose—Dulcin—exists in *melampyrum nemorosum*. It forms colorless, transparent prisms, fuses at 182° , is odorless, faintly sweet, neutral in reaction, and optically inactive. It is subject to decompositions very similar to those to which mannite is subject, yielding **dulcitan**, $C_6H_{12}O_5$.

Heptatomic, Octatomic and Nonatomic Alcohols, containing respectively seven, eight and nine hydroxyls, are also known.

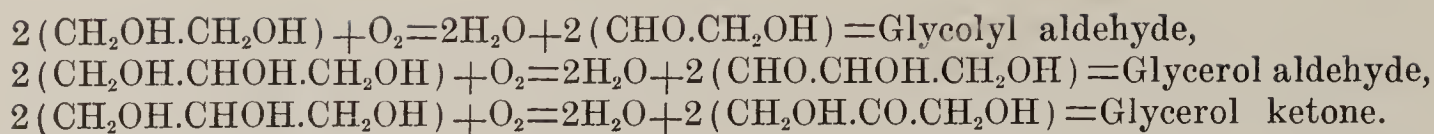
All polyatomic alcohols in solutions alkalized with caustic soda, when agitated with benzoyl chloride, form insoluble benzoic esters, and, under proper conditions, the separation is quantitative, a fact which is utilized for their separation. The diamines behave similarly with benzoyl chloride.

ALDEHYDES AND KETONES.

The pure aldehydes and ketones, containing only CHO or CO and hydrocarbon groups, are to be considered rather as the second products of oxidation of the paraffins than as the first products of oxidation of the alcohols, primary or secondary. While the distinction is not material with the aldehydes derivable from the monoatomic alcohols, it is so with similar derivatives of alcohols of higher atomicity and with the ketones, which may be either pure aldehydes or ketones, or, if they retain alcoholic groups, substances of mixed function: aldehyde-alcohols and ketone-alcohols. Thus from the hydrocarbons the following may be derived:



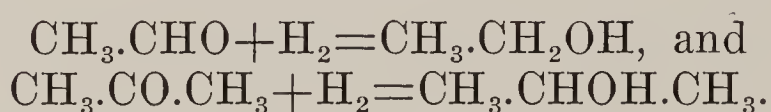
and from the alcohols not only the above, but also substances such as



The aldehydes and ketones are isomeric with each other and also with the alkyl alcohols, $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$, and the methylene oxides, $(\text{CH}_2)_x:\text{O}$.

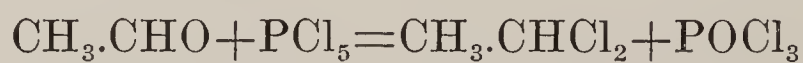
Both aldehydes and ketones contain the carbonyl group CO , which in the ketone is united to two alkyls, $\text{CH}_3.\text{CO}.\text{CH}_3$; and in the aldehyde to one alkyl and a hydrogen atom, $\text{CH}_3.\text{CO}.\text{H}$.

Because of the presence of this oxygen atom, doubly linked to carbon, both aldehydes and ketones form addition products with hydrogen, the former to produce primary, and the latter secondary alcohols:

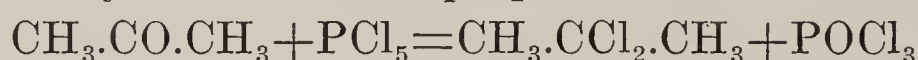


The aldehydes, in which the $\text{C}:\text{O}:$ is in a terminal group, also form other addition products mentioned below.

Aldehydes and ketones are acted upon by phosphorus pentachloride to form compounds in which oxygen is replaced by the halogen. Thus acetic aldehyde yields ethidene chloride, or dichloroethane.

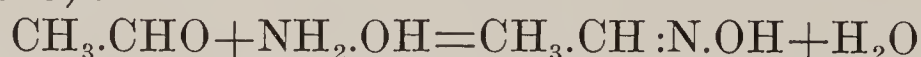


And acetone yields β dichloropropane:



Aldehydes and ketones are acted upon by alkyl magnesium halides to produce secondary and tertiary alcohols (p. 290).

All aldehydes and ketones condense with hydroxylamine to form oximes (p. 320):



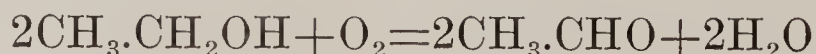
and with phenylhydrazine to form hydrazones and osazones (p. 380). Both of these reactions are extensively used for the identification of substances containing the $\text{C}:\text{O}:$ group.

The aldehydes and ketones may be considered as derivatives of formic aldehyde, $\text{O}:\text{C} \begin{smallmatrix} \text{H} \\ \diagup \diagdown \\ \text{H} \end{smallmatrix}$, alkyls being substituted for one H atom only in the aldehydes: $\text{O}:\text{C} \begin{smallmatrix} \text{CH}_3 \\ \diagup \diagdown \\ \text{H} \end{smallmatrix}$, and for both in the ketones: $\text{O}:\text{C} \begin{smallmatrix} \text{CH}_3 \\ \diagup \diagdown \\ \text{CH}_3 \end{smallmatrix}$.

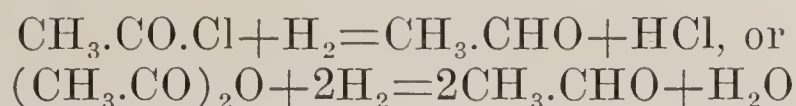
ALDEHYDES.

The name "aldehyde" is a contraction of "alcohol dehydrogenatum," derived from the method of formation of these bodies by removal of hydrogen from alcohol.

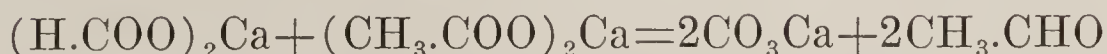
The aldehydes are formed: (1) By the limited oxidation of the corresponding alcohols:



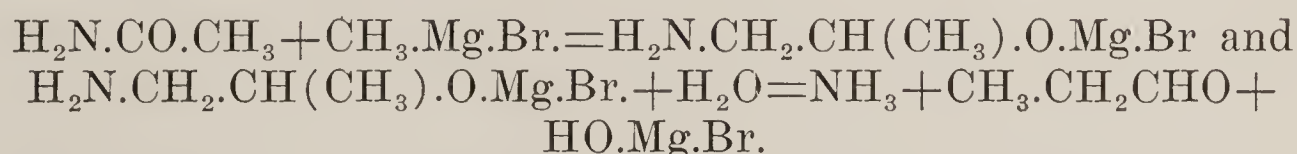
(2) By the action of nascent hydrogen upon the corresponding acidyl chlorides or anhydrides:



(3) By the distillation of a mixture of calcium formate and the Ca salt of the corresponding acid:

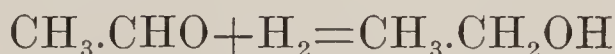


(4) By the action of alkyl magnesium halides upon primary amides, and hydrolysis of the product. Thus propionic aldehyde is produced from acetamide:

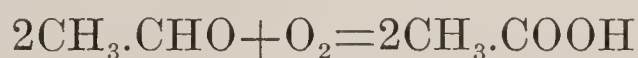


With formamide secondary reactions occur, but with its bisubstituted derivatives, $\text{R}_2\text{N}.\text{CHO}$, the formation of aldehydes proceeds normally.

The aldehydes, being intermediate between the alcohols and acids, are readily converted into the former by the action of reducing agents:

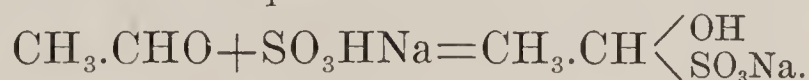


Or into the latter by oxidation:

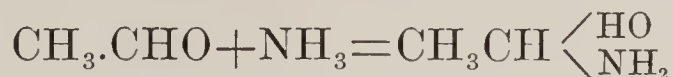


The facility with which the aldehydes are oxidized renders them active reducing agents.

They combine with the monometallic alkaline sulphites to form crystalline compounds, whose formation is frequently resorted to for their separation and purification:



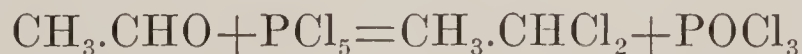
They unite directly with ammonia to produce crystalline compounds called **aldehyde ammonias** (p. 319):



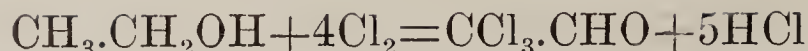
Chlorine and bromine displace the hydrogen of the aldehydic group with formation of acidyl chlorides or bromides:



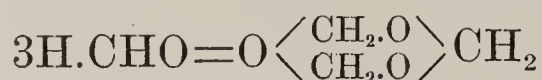
The oxygen of the same group may be displaced by chlorine, by the action of phosphorus pentachloride, with formation of paraffin dichlorides:



By indirect means compounds may be also obtained in which the hydrogen of the hydrocarbon group is substituted by chlorine, as chloral is obtained from ethylic alcohol:



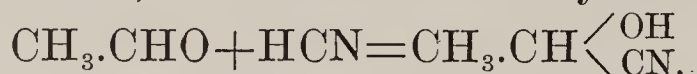
The aldehydes polymerize readily, forming cyclic compounds, as trioxymethylene is formed by formic aldehyde:



Or two aldehyde molecules may condense, by union through carbon atoms, to form **oxyaldehydes**, as aldol is formed by condensation of acetic aldehyde:

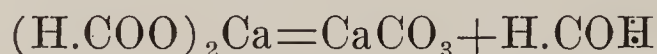


Hydrocyanic acid combines with the aldehydes (and ketones) to produce **oxycyanides**, or nitriles of the oxyacids:



which, in turn, are decomposable by acids or alkalies with formation of the α -oxyacids.

Methanal—Formaldehyde— $\text{H}.\text{CHO}$ —30—is formed when air charged with vapor of methylic alcohol is passed over an incandescent platinum wire. It is also produced by the dry distillation of calcium formate:



By strong cooling, it condenses to a colorless liquid, which boils at -21° . It has a sharp, penetrating odor, and is an active germicide. It is extensively used as an antiseptic and disinfectant, either in the gaseous form or in aqueous solution. The commercial **formaline** is a 40 per cent. solution.

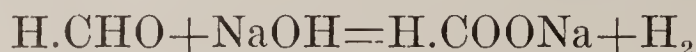
Formic aldehyde is probably produced as an intermediate product in plant nutrition, when carbon dioxide is decomposed by the green pigment, **chlorophyll**, under the influence of sunlight, with liberation of oxygen: $\text{CO}_2 + \text{H}_2\text{O} = \text{H}.\text{CHO} + \text{O}_2$, and when so produced it may readily polymerize to form hexoses (p. 237): $6\text{H}.\text{CHO} = \text{C}_6\text{H}_{12}\text{O}_6$.

Formaldehyde polymerizes with great readiness by moderate elevation of temperature to form **paraformaldehyde**, or **trioxymethylene**, $\text{O} \left\langle \begin{array}{c} \text{CH}_2.\text{O} \\ \text{CH}_2.\text{O} \end{array} \right\rangle \text{CH}_2$, which is also obtained as a crystalline substance, fusing at 152° , insoluble in H_2O , alcohol and ether, by distilling glycollic acid with H_2SO_4 , or by the action of silver oxalate or oxide on methene iodide: $\text{CH}_2\text{I}_2 + \text{Ag}_2\text{O} = \text{H}.\text{CHO} + 2\text{AgI}$.

Formic aldehyde reacts with a great variety of substances, and, in reactions at elevated temperatures may advantageously be replaced by the solid trioxymethylene, which is then dissociated. Like all aldehydes (and it is doubly an aldehyde: $\text{O}:\text{C} \left\langle \begin{array}{c} \text{H} \\ \text{H} \end{array} \right\rangle$), it is an active reducing agent. With caustic alkalies it forms methyl alcohol and a formate:



Or, in the presence of CuO , a formate and hydrogen:

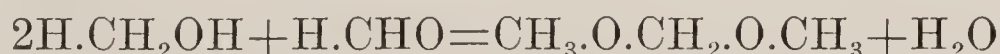


Calcium hydroxide and other basic hydroxides, by prolonged contact, cause its polymerization to **formose**: $6\text{H}.\text{CHO}=\text{C}_6\text{H}_{12}\text{O}_6$. With ammonia it forms hexamethylene tetramine; and with ammoniacal salts it forms a variety of complex amines and nitriles.

An extremely valuable property of formic aldehyde is the facility with which it parts with its oxygen atom, by reason of which it readily enters into condensations, uniting other molecule-remainders through the bivalent group CH_2 .

A condensation is the formation of a new molecule by the union of the remainders of two or more others, with the splitting off of water, alcohol, or some other substance. A condensation differs from a polymerization in that in the latter nothing is split off, and all the substances involved are polymeres of each other. Sometimes condensations are effected by simple contact of the reacting substances at more or less elevated temperatures; but, more usually, the presence of another substance, acting as a contact agent, is required. Substances acting in this manner are quite numerous, and are called **condensing agents**. Probably the most important are aluminium, ferric and zinc chlorides, hydrochloric and sulphuric acids, sodium acetate and ethylate, pyridine, and piperidine.

As examples of the simplest condensations with formic aldehyde we may mention the two following: With alcohols it condenses to produce formals:



With secondary amines it condenses to form alkyl diamines:



an action which is particularly marked with aromatic amines:



Other instances of the condensing action of formic aldehyde will be considered later.

The presence of formic aldehyde, which is now frequently added to milk and other articles of food, may be recognized by the following reactions, after distillation, if necessary: (1) Heat with 0.5 cc. dimethylaniline and a few drops H_2SO_4 on the water-bath for half an hour; add excess of alkali; expel excess of dimethylaniline with a current of steam; filter; place the filter in a porcelain capsule and moisten it with acetic acid; add a trace of lead peroxide, and warm: an intense blue color. (2) Add the liquid (distillate) to an equal volume of aqueous solution of aniline (3:1000): a white ppt. (3) Dissolve 0.01 morphine hydrochloride in 1 cc. concentrated H_2SO_4 , and mix two drops of this and suspected solutions: an intense rose-violet color.

Ethanal—Acetaldehyde—Acetic Aldehyde— $\text{CH}_3.\text{CHO}$ — 44—is formed in all reactions in which alcohol is deprived of H without introduction of O. It is prepared by distilling from a capacious retort, connected with a well-cooled condenser, a mixture of H_2SO_4 ,

6 pts.; H_2O , 4 pts.; alcohol, 4 pts., and powdered manganese dioxide, 6 pts. The product is redistilled from calcium chloride below 50° . The second distillate is mixed with two volumes of ether, cooled by a freezing mixture, and saturated with dry NH_3 ; there separate crystals of **aldehyde ammonia**, $\text{CH}_3.\text{CH} \begin{smallmatrix} \text{NH}_2 \\ \text{OH} \end{smallmatrix}$, which are washed with ether, dried and decomposed in a distilling apparatus, over the water-bath, with the proper quantity of dilute H_2SO_4 ; the distillate is finally dried over calcium chloride and rectified below 35° .

Acetic aldehyde is also formed by heating acetylene with vapor of water:



Aldehyde is a colorless, mobile liquid; has a strong, suffocating odor; sp. gr. 0.790 at 18° ; boils at 21° ; soluble in all proportions in water, alcohol and ether. If perfectly pure, it may be kept unchanged; but if an excess of acid has been used in its preparation, it gradually decomposes. When heated to 100° it is decomposed into water and crotonic aldehyde:



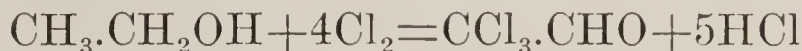
In the presence of nascent H, aldehyde takes up H_2 , and regenerates alcohol. Cl converts it into acetyl chloride, $\text{C}_2\text{H}_3\text{O}.\text{Cl}$, and other products. Oxidizing agents convert it into acetic acid. At the ordinary temperature H_2SO_4 ; HCl ; and SO_2 convert it into a colorless liquid called **paraldehyde** $(\text{C}_2\text{H}_4\text{O})_3$, which boils at 124° , and is more soluble in cold than in warm water. The same reagents, acting upon aldehyde at temperatures below 0° convert it into **metaldehyde** $(\text{C}_2\text{H}_4\text{O})_n$. When heated with potassium hydroxide, aldehyde becomes brown, a brown resin separates, and the solution contains potassium formate and acetate.

Vapor of aldehyde, when inhaled in a concentrated form, produces asphyxia, even in comparatively small quantity. When diluted with air it is said to act as an anesthetic. When taken internally it causes sudden and deep intoxication, and it is to its presence that the first products of the distillation of spirits of inferior quality owe in a great measure their rapid, deleterious action.

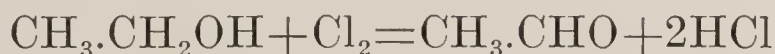
Trichloraldehyde—Chloral— $\text{CCl}_3.\text{CHO}$ —147.5—is one of the final products of the action of Cl upon alcohol, and is obtained by passing dry Cl through absolute alcohol to saturation; applying heat toward the end of the reaction, which requires several hours for its completion. The liquid separates into two layers; the lower is removed and shaken with an equal volume of concentrated H_2SO_4 and again allowed to separate into two layers; the upper is decanted; again mixed with H_2SO_4 , from which it is distilled; the distillate is treated with quicklime, from which it is again distilled, that portion which passes over between 94° and 99° being collected. It sometimes hap-

pens that chloral in contact with H_2SO_4 is converted into a modification, insoluble in H_2O , known as **metachloral**; when this occurs it is washed with H_2O , dried and heated to 180° , when it is converted into the soluble variety, which distils over.

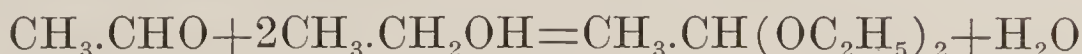
The formation of chloral from alcohol does not progress according to the simple equation:



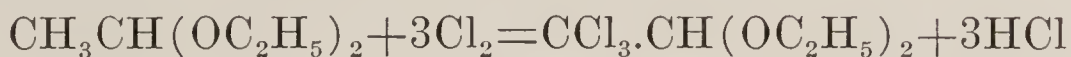
but passes through several stages. First, the alcohol is oxidized to aldehyde:



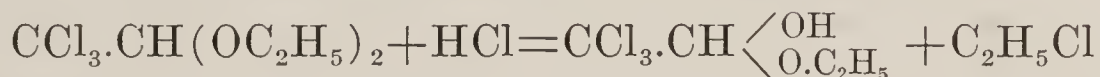
This reacts with alcohol to produce acetal:



This is then converted into trichloroacetal:



This, by the action of the hydrochloric acid formed in the last reaction, yields chloral alcoholate and ethyl chloride:

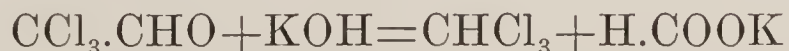


And from the former chloral is liberated by sulphuric acid:

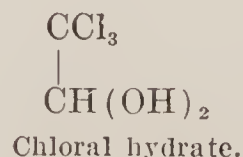
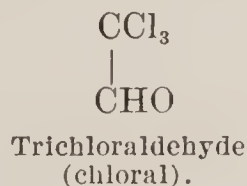
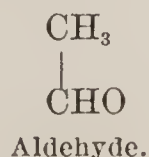


Chloral is a colorless liquid, unctuous to the touch; has a penetrating odor and an acrid, caustic taste; sp. gr. 1.502 at 18° , boils at 97° , very soluble in water, alcohol, and ether; dissolves Cl, Br, I, S, and P. Its vapor is highly irritating. It distils without alteration.

Although chloral has not been obtained by the direct substitution of Cl for H in aldehyde, its reactions show it to be an aldehyde. It forms crystalline compounds with the bisulphites; it reduces solutions of silver nitrate in the presence of NH_3 ; with nascent H it regenerates aldehyde; oxidizing agents convert it into trichloroacetic acid. Alkaline solutions decompose it with formation of chloroform and a formate:



With a small quantity of H_2O chloral forms a solid, crystalline hydrate, heat being at the same time liberated. This hydrate has the composition $\text{C}_2\text{HCl}_3\text{O}.\text{H}_2\text{O}$, and its constitution, as well as that of chloral itself, is indicated by the formulæ:



Chloral Hydrate—Chloralum hydratum—Chloral—(U. S. P.)— is a white, crystalline solid; fuses at 57° ; boils at 98° , at which temperature it suffers partial decomposition into chloral and H_2O ;

volatilizes slowly at ordinary temperatures; is very soluble in H_2O ; neutral in reaction; has an ethereal odor, and a sharp, pungent taste. Concentrated H_2SO_4 decomposes it, with formation of chloral and chloralide, $\text{C}_5\text{H}_2\text{Cl}_6\text{O}_3$. [chloralide, or chloraldide is trichlorethidene trichloroacetic ester: $\text{CCl}_3\text{CH} \begin{smallmatrix} \text{O} \\ \diagup \text{COO} \diagdown \end{smallmatrix} \text{CH.CCl}_3$]. HNO_3 converts it into trichloroacetic acid. When pure it gives no precipitate with silver nitrate solution, and is not browned by contact with concentrated H_2SO_4 . Under the influence of sunlight it is violently decomposed by potassium chlorate, which oxidizes it in part to trichloroacetic acid; chlorine, phosgene gas, carbon dioxide, and chloroform are given off, and after a time, crystals of potassium trichloroacetate separate from the cooled mixture.

Chloral also combines with alcohol, with elevation of temperature, to form a solid, crystalline body—chloral alcoholate: $\text{CCl}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \diagup \text{O} \end{smallmatrix} \text{C}_2\text{H}_5$.

Action of Chloral Hydrate upon the Economy.—Although it was the ready decomposition of chloral into a formate and chloroform which first suggested its use as a hypnotic to Liebreich, and although this decomposition was at one time believed to occur in the body under the influence of the alkaline reaction of the blood, more recent investigations have shown that the formation of chloroform from chloral in the blood is, to say the least, highly improbable, and that chloral has, in common with many other chlorinated derivatives of this series, the property of acting directly upon the nerve-centers.

Neither the urine nor the expired air contains chloroform when chloral is taken internally; and when taken in large doses, chloral appears in the urine. The fact that the action of chloral is prolonged for a longer period than that of the other chlorinated derivatives of the fatty series is probably due, in a great measure, to its less volatility and less rapid elimination.

When taken in overdose, chloral acts as a poison; a strong aqueous solution is frequently added by criminals to intoxicants to deprive their victims of consciousness (*knock-out drops*).

No chemical *antidote* is known. The treatment should be directed to the removal of any chloral remaining in the stomach by the stomach tube, and to the maintenance or restoration of respiration.

In fatal cases of poisoning by chloral that substance may be detected in the blood, urine, and contents of the stomach by the following method: the liquid is rendered strongly alkaline with potassium hydroxide: placed in a flask, which is warmed to $50^\circ\text{--}60^\circ$, and through which a slow current of air, heated to the same temperature, is made to pass; the air, after bubbling through the liquid, is tested for chloroform by the methods described on p. 206. As chloral distils with vapor of water from acid solutions, and as it gives the same reactions as chloroform, except that with the resorcinol reaction it gives a brilliant green fluorescence (p. 207), the presence of chloral as such can only be positively demonstrated by extraction of the crystals of the hydrate by ether, and spontaneous evaporation of the ethereal solution.

Acetals—Formals.—These are ester-like bodies corresponding to the hypothetical aldehyde hydrates: $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \diagup \text{OH} \end{smallmatrix}$, which are themselves incapable of existence, except they contain a halogen, as in chloral hydrate: $\text{CCl}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \diagup \text{OH} \end{smallmatrix}$.

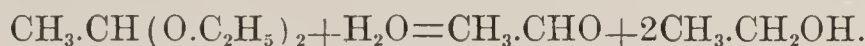
The acetals have the general formula: $R'.CH \begin{smallmatrix} \diagup OR' \\ \diagdown OR' \end{smallmatrix}$, and the formals the structure: $CH_2 \begin{smallmatrix} \diagup OR' \\ \diagdown OR' \end{smallmatrix}$, in which R' represents an alkyl. The acetals are produced by oxidation of the alcohols by MnO_2 and H_2SO_4 . Thus



and by other methods. The formals are formed by condensation, in presence of H_2SO_4 , or of $FeCl_3$, of alcohols and formic aldehyde:



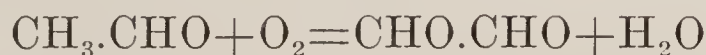
The formation of acetals and formals is utilized in the preparation of certain aldehydes, such as glyceric aldehyde. By hydrolyzing agents, as by heating with aqueous HCl , they are split into their components:



Methylal—Formal— $CH_2 \begin{smallmatrix} \diagup OCH_3 \\ \diagdown OCH_3 \end{smallmatrix}$ —76—is formed by distilling a mixture of MnO_2 , methyl alcohol, H_2SO_4 and H_2O . It is a colorless liquid; sp. gr. 0.8551 at 17° ; boiling at 42° ; soluble in H_2O , alcohol, and oils. It has a burning, aromatic taste, and an odor resembling those of chloroform and acetic acid. It has been used as a hypnotic.

Acetal— $CH_3.CH \begin{smallmatrix} \diagup OC_2H_5 \\ \diagdown OC_2H_5 \end{smallmatrix}$ —104—a colorless liquid, boils at 104° , sp. gr. 0.8314; sparingly soluble in H_2O , readily in alcohol; obtained by heating a mixture of aldehyde, alcohol and glacial acetic acid, or in the same manner as formal, using ethylic in place of methylic alcohol.

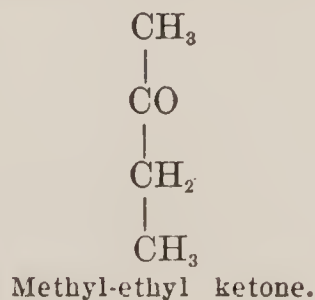
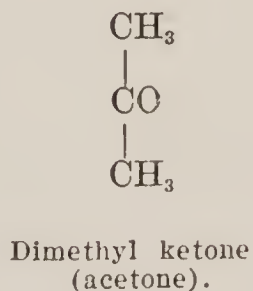
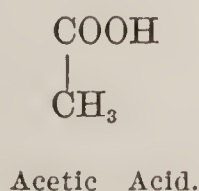
Dialdehydes—containing two CHO groups, such as **Glyoxal**— $CHO.CHO$, are also known. Glyoxal is formed by the limited oxidation of acetic aldehyde by nitric acid:



But it has not been obtained pure, containing oxalic and formic acids as impurities. It is very soluble in water, and has the chemical properties common to the aldehydes.

KETONES OR ACETONES.

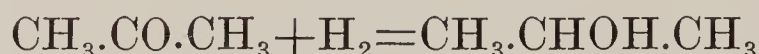
The ketones, or acetones, contain the group $C:O$, linking two hydrocarbon groups; or they may be considered as derived from the hydrocarbons by substitution of O for H_2 in a CH_2 group. The **mono-ketones** contain one CO group, the **diketones** two, etc. The (CO) group also occurs in the aldehydes, in which, however, it is linked with H , $(O:C.H)'$, and in the carboxyl group, in which it is linked with OH , $(O:C.OH)'$, in both cases occupying a terminal position with reference to other C atoms, while in ketones, ketonic acids, etc., its position is intermediate. Ketones are **symmetrical** if the two alkyls united by CO are similar, **unsymmetrical** if they are different:



Ketones are isomeric with and closely allied to the aldehydes, from which they differ chiefly in that: (1) They are not so easily oxidized, do not reduce alkaline solutions of silver salts, and, on oxidation, split at the CO group to form a carboxylic acid or acids, or ketones, of less carbon content:



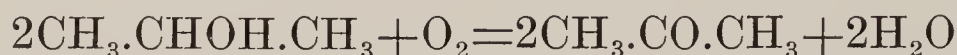
(2) Nascent hydrogen converts them into secondary alcohols by addition:



(3) The ketones do not polymerize.

(4) Only those ketones which contain a methyl group form crystalline compounds with alkaline bisulphites.

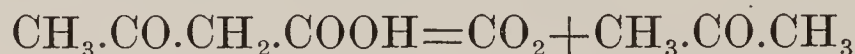
The monoketones are produced: (1) By oxidation of the secondary alcohols:



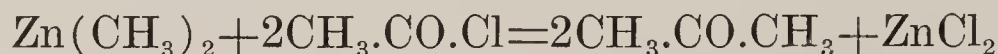
(2) By distillation of the calcium salts of the fatty acids:



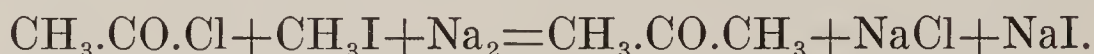
(3) By decomposition of ketonic acids:



(4) By the interaction of zinc alkyls and acidyl halides:



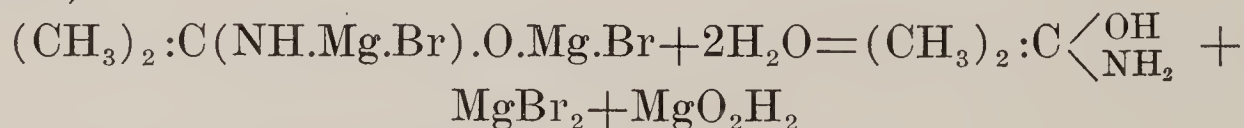
(5) By the action of sodium upon a mixture of acidyl and alkyl halides:



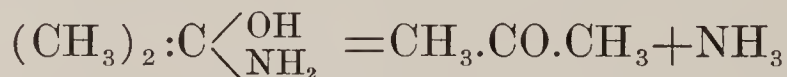
(6) By the action of alkyl magnesium halides upon primary amides, and hydrolysis of the product, the reactions being three in number. First, a condensation:



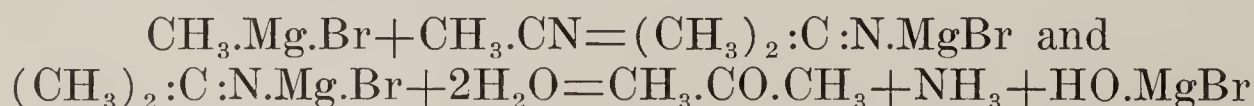
Second, the hydrolysis of this with the formation of an oxyamine (p. 296):



And, finally, the deamidation of the oxyamine:

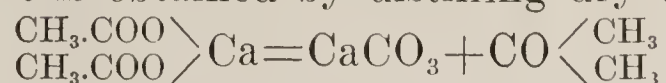


(7) By the action of alkyl magnesium halides upon nitriles, and hydrolysis of the products:



Acetone — Dimethyl Ketone — Propanon — $\text{CO} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$ — 58 — is formed as one of the products of the dry distillation of the acetates; by the decomposition of the vapor of acetic acid at a red heat; by

the dry distillation of sugar, tartaric acid, etc.; and in a number of other reactions. It is obtained by distilling dry calcium acetate:



It is also formed in large quantity in the preparation of aniline.

It is a limpid, colorless liquid; sp. gr. 0.921 at 18°; boils at 56°; soluble in H₂O, alcohol and ether; has a peculiar ethereal odor and a burning taste; is a good solvent of resins, fats, camphor, gun-cotton; readily inflammable. It forms crystalline compounds with the alkaline bisulphites. Cl and Br, in the presence of alkalis, convert it into chloroform or bromoform; Cl alone produces with acetone a number of chlorinated products of substitution. Certain oxidizing agents transform it into a mixture of formic and acetic acids; others into oxalic acid.

Acetone has been found to exist in the blood and urine in certain pathological conditions, and notably in diabetes. The peculiar odor exhaled by diabetics is produced by this substance, which has also been considered as being the cause of the respiratory derangements and coma which frequently occur in the last stage of the disease.

That acetone exists in the blood in such cases is certain: it is not certain, however, that its presence produces the condition designated as **acetonemia**. It can hardly be doubted that the acetone thus existing in the blood is indirectly formed from diabetic sugar, and it is probable also that a complex acid, known as **ethyldiacetic**, C₆H₉O₃H, is formed as an intermediate product.

See aromatic ketones.

Diketones, containing two CO groups, such as CH₃.CO.CO.CH₃, **triketones**, such as CH₃.CO.CO.CO.CH₃, and **tetraketones**, such as CH₃.(CO)₄.CH₃, are also known.

CARBOHYDRATES.

The definition of the term **carbohydrate** as “a substance of unknown constitution composed of carbon, hydrogen and oxygen, in which the oxygen and hydrogen are in the same proportion as in water” was self-destructive so soon as the constitution of these substances should become known, as it now has. Yet the first words of the definition were necessary to exclude substances such as acetic acid, C₂H₄O₂, which would otherwise accord with the definition, yet were never considered as carbohydrates. But, while the sugars and starches have been thus removed from the “miscellaneous” residuum of our chemical classification, they are still conveniently referred to as carbohydrates in physiological chemistry.

The simplest of the carbohydrates are oxyaldehydes or ketols in which all the groups, other than the aldehyde or ketone groups, are primary or secondary alcoholic groups; and the more complex consist of two or more molecules of the simpler forms, united with elimination of water.

The carbohydrates are classified into:

Monosaccharides, or **Monoses**—which do not yield any other sugar or sugars by the action upon them of dilute acids (glucose, fructose, galactose, etc.);

Disaccharides, or **Saccharobioses**—which, under the influence of dilute acids, take up H_2O and yield two other sugar molecules (saccharose, lactose, maltose, etc.);

Trisaccharides, or **Saccharotrioses**—which, under the same influence, take up $2\text{H}_2\text{O}$ and yield three other sugar molecules; and

Polysaccharides—which, under the same influence, take up more than $2\text{H}_2\text{O}$, and yield more than three sugar molecules (starches, gums, celluloses, etc.).

The disaccharides, trisaccharides, and polysaccharides may be considered as produced by the fusion of two or more monosaccharide molecules with elimination of one or more molecules of water.

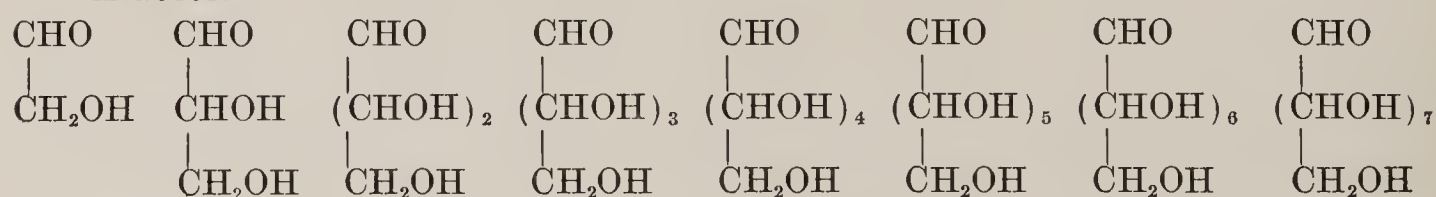
Those carbohydrates which contain the ketone group, CO , are called **ketoses**, those containing the aldehyde group, CHO , **aldoses**. The names of all carbohydrates terminate in **ose**.

MONOSACCHARIDES—MONOSES.

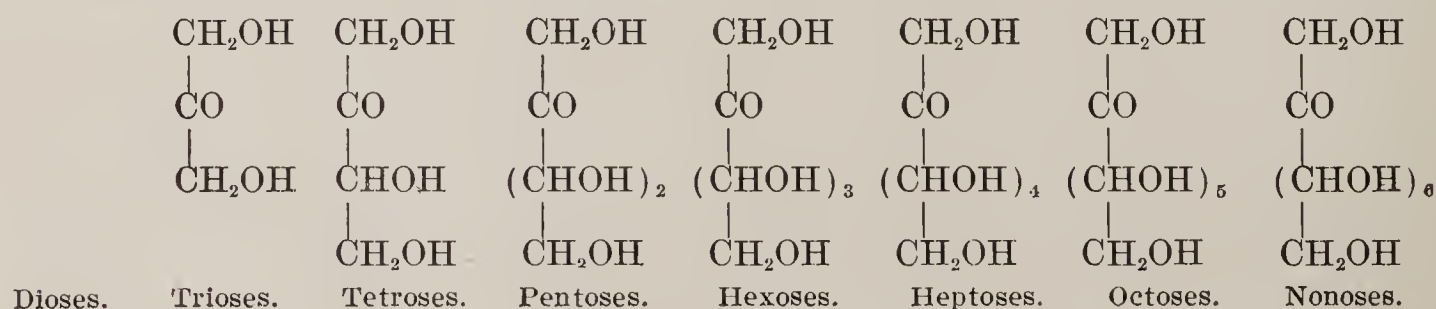
Monosaccharides are **dioses**, **trioses**, **tetroses**, **pentoses**, **hexoses**, **heptoses**, **octoses** or **nonoses** according as they contain from two to nine carbon atoms. (See table below.)

The monosaccharides are neutral substances, sweet, odorless, white, insoluble in ether, sparingly soluble in alcohol, and readily soluble in water. Like all aldehydes and ketones, they are readily oxidized, and in their oxidation act as reducing agents. It is upon this quality that the several "reduction tests," such as Trommer's, Fehling's, Boettger's, etc., are based. Another quality of the monosaccharides, utilized for their separation and identification, is that they all give crystalline precipitates of substances called **osazones** when their solutions, acidulated with acetic acid, are heated with phenylhydrazine, $\text{C}_6\text{H}_5\text{H}:\text{N}:\text{N}:\text{H}_2$. The trioses, hexoses and nonoses are capable of alcoholic fermentation, the others are not.

Aldoses.



Ketoses.



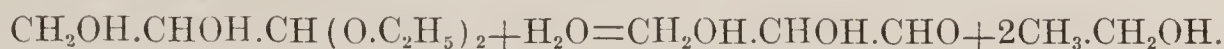
DIOSES, TRIOSSES, TETROSES AND PENTOSES.

Glycolyl aldehyde, $\text{CH}_2\text{OH}\cdot\text{CHO}$, is the only **diose** possible. It is produced by the action of baryta water upon brom-acetaldehyde.

Of the two possible trioses **Glyceric aldehyde** is obtained by starting from acrolein acetal. This is oxidized to glyceric acetal:



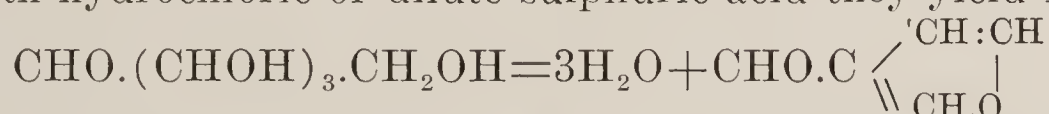
which is then hydrolyzed:



Glycerol ketone, or **dioxyacetone**, $\text{CH}_2\cdot\text{OH}\cdot\text{CO}\cdot\text{CH}_2\text{OH}$, has also been obtained synthetically. The aldehyde and ketone are formed together when glycerol is oxidized by dilute nitric acid.

Similarly **erythrose** is a mixture of the two **tetroses**, $\text{CHO}\cdot(\text{CHOH})_2\cdot\text{CH}_2\text{OH}$ and $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CO}\cdot\text{CH}_2\text{OH}$, formed by oxidation of erythrol by dilute nitric acid.

The **pentoses** hitherto described are all aldo-pentoses, $\text{C}_4\text{H}_5\cdot(\text{OH})_4\cdot\text{CHO}$, although keto-pentoses probably also exist. When distilled with hydrochloric or dilute sulphuric acid they yield furfurole:



a reaction which is utilized for their quantitative determination.

Arabinose is a pentose obtained by the action of dilute sulphuric acid upon cherry gum. **Xylose**, or wood sugar, is produced by boiling wood-gum with dilute acid. **Ribose** is a synthetic product. **Rhamnose**, or **Isodulcite**, **Chinovose**, and **Fucose** are methyl-pentoses: $\text{CH}_3(\text{CHOH})_4\cdot\text{CHO}$, obtained by the decomposition of certain glucosides or from sea weeds. These pentoses result from the hydrolysis of pentosanes, polysaccharides occurring as gums in plants. Pentoses have also been found in the urine, particularly in diabetes and after the use of certain fruits containing pentosanes. They are also among the products of decomposition of certain nucleoproteids. Pentoses, when warmed with hydrochloric acid in presence of phloroglucin, give a fine red color, and a sharp absorption band near the Na line.

HEXOSES—GLUCOSES.

In this class are included some well-known sugars, such as glucose and fructose, which occur free in the vegetable world. They exist in ether-like combination in many of the **glucosides**.

They are mostly sweet, crystalline substances, very soluble in water, and difficultly soluble in alcohol. They are formed by (1) the hydrolysis of the di- and polysaccharides:

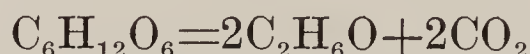


(2) By oxidation of the corresponding hexatomic alcohol.

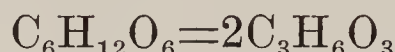
(3) By reduction of the lactones of the monocarboxylic acids.

They exhibit the usual reactions of the alcohols and those of the aldehydes or ketones. On reduction they produce hexatomic alcohols;

and on oxidation they yield monocarboxylic acids. Their alcoholic hydrogen is replaceable by certain metals with formation of **saccharates**, corresponding to the alcoholates. With acids they yield esters. They form **osazones** with phenylhydrazine. Some are very prone to alcoholic fermentation:



while others readily undergo lactic fermentation:



Being polyatomic alcohols, the hexoses form insoluble benzoic esters when their alkaline solutions are shaken with benzoyl chloride.

Of the described hexoses, mannose, glucose, gulose, idose, galactose and talose are aldoses; fructose and sorbinose are ketoses.

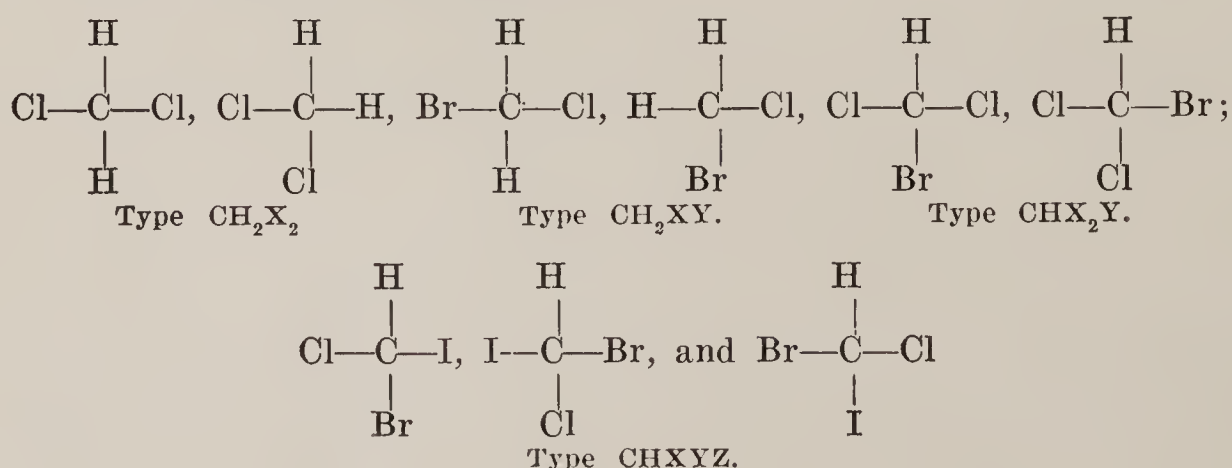
Optical Activity.—All of the hexoses exist in three isomerides, differing from each other in their action upon polarized light. One of these rotates the plane of polarization to the right, and is designated as the dextro-, or d-compound; another is lævogyrous and is designated as the lævo-, or l-compound, while the third is inactive, and is distinguished by the symbol (d+l).

Stereoisomerism, or Space Isomerism.—The graphic formulæ indicate the structure of the molecule only partially; they show that certain atoms in the molecule are attached to some of their fellows more closely than to others, but they give no indication of the positions which the atoms occupy in space

with regard to each other. The expression $\begin{array}{c} \text{H} \backslash \\ \text{C} - \text{O} - \text{H} \\ \text{H} / \end{array}$, the most completely

detailed graphic representation of that group, indicates at the most that the two hydrogen atoms are attached to one side of the carbon atom, while the hydroxyl is attached to another. **Stereochemistry** is that branch of chemistry treating of the relations of the atoms to each other *in space*. It has been greatly developed in recent years and affords, among other things, the first rational explanation of the cause of the differences in the optical activity of the hexoses, as well as of lactic and tartaric acids, and of many other substances.

If we suppose that differences in the relative positions which atoms or groups attached to carbon atoms occupy with relation to each other produce different compounds (see Place Isomerism, p. 260, Orientation, p. 337); and if we also suppose that the four valences of the carbon atom act in a plane and at right angles to each other, a vast number of space-isomerides of the di- and poly-substituted derivatives of the aliphatic hydrocarbons would exist, no representatives of which are, however, known. For example, marsh-gas would yield two isomerides of each of the types: CH_2X_2 , CH_2XY and $\text{CH}(\text{X})_2\text{Y}$, and three isomerides of the type CHXYZ , in which X, Y, and Z represent any three univalent atoms or radicals, thus:



But only one representative of each of these types is known. Therefore the usual graphic representation of the valences of the carbon atom as above, while convenient, is not *spatially* consistent with fact, and the four valences of the carbon atom are not exerted in one plane.

The suggestion of Van't Hoff (following the somewhat similar idea of Kekulé) that the valences of the carbon atom are represented by considering it as occupying the interior of a regular tetrahedron, the solid angles of which indicate the direction of its valences (Fig. 18, A), taken in connection with the hypothesis of an **asymmetric carbon atom**, affords a rational explanation of the facts just cited, and of the differences in the optical properties of the substances mentioned.

Admitting the regular tetrahedron to represent the arrangement of the valences of the carbon atom, it follows that all carbon atoms, two of whose valences are satisfied by the same kind of univalent atom or group, and the other two by two constant but dissimilar univalents, must be symmetrical. The two similar univalents must occupy the summits at the extremities of some one crest, and the only possible variation in arrangement of the other two is in their position with regard to this crest. Thus B and C, Fig. 18, although dissimilar in the position in which they are placed, become perfectly symmetrical when either one is rotated through 180 degrees. But when all four of the carbon valences are satisfied by different univalents two arrangements are possible, producing two molecular groups which are unsymmetrical in whatever position they may be placed. Thus D and E, Fig. 18, are unsymmetrical in the positions in which they are represented, and remain so, however their positions may be changed. A carbon atom attached to four different univalents is called an **asymmetric carbon atom**.

In graphic formulæ asymmetric carbon atoms are designated by the italic *C*, or by an asterisk, *C**. Substances containing an asymmetric carbon atom exist in three optical isomeres: *dextrogyrous* (d), *laevogyrous* (l), and *optically inactive*, or *racemic* (d+l or i, or r).

The structure of the four isomeric tartaric acids was first explained under the hypothesis of the asymmetric carbon atom. Let it be assumed that two asymmetric carbon atoms, with their attached groups or atoms, exert a "directing influence" upon each other, and that, being attached to each other at one point only, they are capable of rotating independently about a common axis (*a. a.* Fig. 18, G), such rotation would then occur in obedience to the

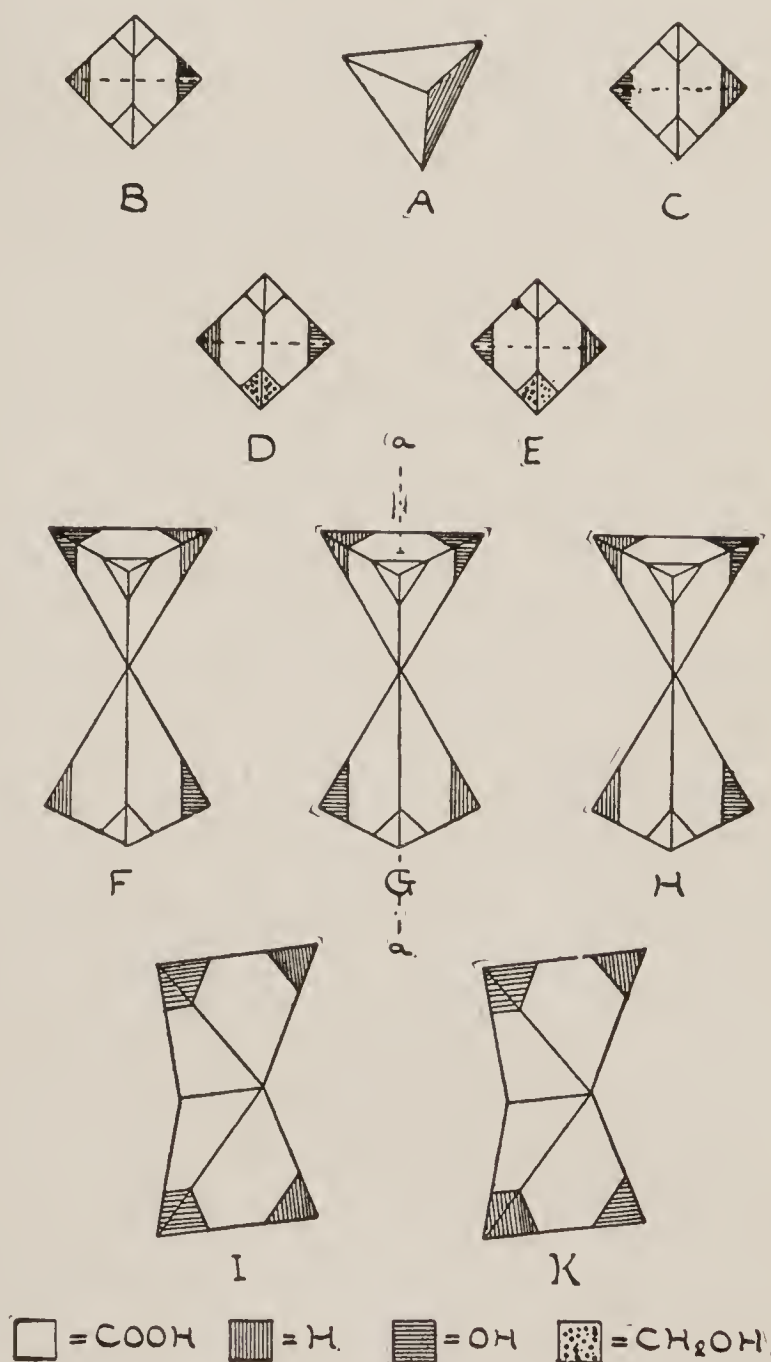
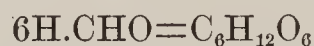


FIG. 18.

directing influence until a condition of equilibrium is reached, in which position the atoms would remain. Assuming this position to be that shown in F, G, and H, Fig. 18, with the two COOH groups in like relation, then the three unsymmetrical arrangements shown in the figure are possible. The first represents the structure of dextro-tartaric acid, G that of lævo-tartaric acid, and H that of meso-tartaric acid, while racemic acid is a combination of dextro- and lævo-tartaric acids.

The tetrahedron representation of the carbon valences adapts itself well also to the explanation of certain isomerides of the ethylene series, in which two carbon atoms are doubly linked together. In these the two carbon atoms being linked together at two points (I and K, Fig. 18) cannot be considered as being capable of rotation, and, if the two other valences of each carbon are satisfied by the same two dissimilar univalents, two positions are possible: I, in which the like univalents are directed to the same side, called the "plane symmetrical configuration," and K, in which they are directed towards opposite sides, called the "axially symmetrical configuration."

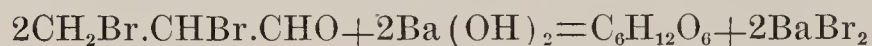
Formose is a synthetic hexose, obtained by polymerization of formic aldehyde:



Acrose is similarly obtained from glyceric aldehyde:



or by the action of barium hydroxide upon acrolein bromide:



Mannose is obtained, as d-, l-, and d+l, mannoses by oxidation of the corresponding mannitols.

Glucose — Grape Sugar — Dextrose — Liver Sugar — Diabetic Sugar—d-Glucose occurs in many sweet fruits and vegetable juices, and in honey, accompanied by fructose; and, in the animal world, in the contents of the intestine, liver, bile, thymus, heart, lungs, blood, and, in small quantity, in the urine. Pathologically, it appears in the saliva, perspiration, feces, and, in largely increased amount, in the blood and urine in diabetes mellitus. It is produced by the decomposition of the polysaccharides and of many of the glucosides, and is manufactured on a large scale by the action of boiling dilute H_2SO_4 upon starch. The commercial product so obtained is either an amorphous; white solid (grape sugar), containing about 60% of true glucose, along with dextrins and the unfermentable **isomaltose**, or **gallisin**, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$; or a thick, colorless syrup (glucose), containing, besides the above, a minute quantity of a nitrogenous body which exerts a solvent action upon coagulated albumin at the body temperature.

d-Glucose has been produced synthetically by the reduction of the lactone of d-gluconic acid.

It crystallizes from its aqueous solutions at the ordinary temperature with difficulty in white, opaque, spheroidal masses containing 1Aq, which fuse at 86° and lose the Aq at 110° . From its concentrated aqueous solution at 30° to 35° , or from its alcoholic solution it crystallizes in hard, anhydrous, crystalline crusts, which fuse at 146° .

It is soluble in all proportions in hot water, is very soluble in cold water, and soluble in alcohol. It is less sweet and less soluble than cane sugar. Its aqueous solutions are dextrogyrous: $[\alpha]_D = +52.6^\circ$ in boiled solutions. Freshly prepared cold aqueous solutions have nearly double that rotary power at first, the value of $[\alpha]_D$ gradually falling to 52.6° in about twenty-four hours. Its osazone, d-glucosazone, crystallizes in needles, fusible at 205° . Its solutions dissolve baryta and lime, with which, as with potash, soda, and the oxides of Pb and Cu, it forms **saccharates**.

l-Glucose is formed by reduction of the lactone of l-gluconic acid. It is in all respects similar to d-glucose except that it fuses at 143° , and its solutions are lævogyrous $[\alpha]_D = -51.4^\circ$.

d+l-Glucose is formed by reduction of d+l-gluconic lactone; or by union of d- and l-glucose. Its solutions are optically inactive.

Galactose is also known in its three modifications. d-Galactose is produced by the hydrolysis of milk sugar and of certain gums. It crystallizes more readily than glucose, is very sparingly soluble in cold alcohol, has a specific rotary power of $[\alpha]_D = +83.33^\circ$, and fuses at 160° . By reduction it yields dulcitol, and by oxidation galactonic acid, $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH}$, and mucic acid, $\text{COOH}(\text{CHOH})_4\text{COOH}$. **Cerebrose**, obtained by the hydrolysis of **cerebrin**, a constituent of nerve tissue, is identical with galactose.

Fructose—Levulose—a ketohexose, exists in the three modifications. *d-Fructose—Fruit sugar*—forms the uncrystallizable portion of the sugar of fruits and of honey, in which it is associated with glucose; it is produced artificially by the prolonged action of boiling water upon **inulin**, a polysaccharide; also, along with an equal quantity of glucose, as one of the constituents of **invert sugar**, by the decomposition of cane sugar; and from d-glucosazone. It crystallizes with great difficulty, fuses at 95° , is very soluble in water, and insoluble in absolute alcohol. Although called d-fructose, because of its formation from d-glucosazone, it is strongly lævorotary: $[\alpha]_D = -71.4^\circ$. It is less readily fermentable than glucose, which it equals in the readiness with which it reduces cupropotassic solutions. With phenylhydrazine it yields d-glucosazone (p. 381).

Sorbinose, also a ketohexose, occurs in the berries of the mountain ash. It does not ferment. Its osazone fuses at 164° .

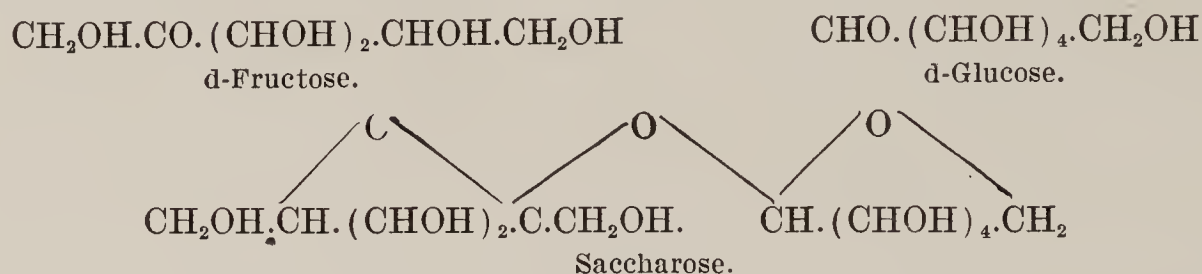
DISACCHARIDES—SACCHAROBIOSES.

Disaccharides consist of two molecules of monosaccharides, united with elimination of H_2O . So far as is known they are all derived from the hexoses, and their formula is consequently $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. They are all capable of yielding two hexose molecules by hydrolysis:

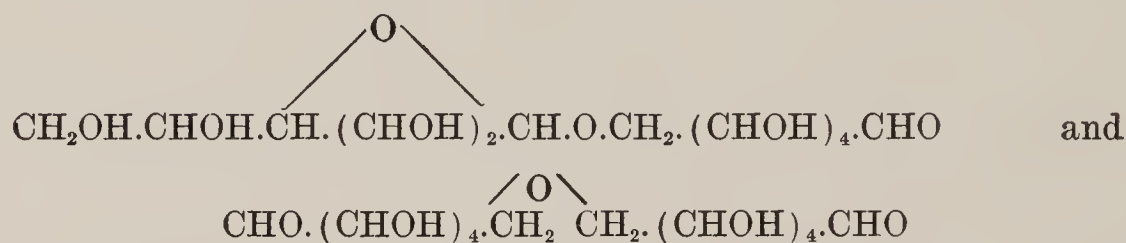


a change which is called “inversion.” The union of the two monosaccharide molecules is either through the aldehyde, ketone, or alcoholic groups. Of the three most important disaccharides, saccharose, lactose and maltose, the first named has no reducing power, and yields no osazone with phenylhydrazine. It therefore contains

no aldehyde or ketone group. When heated with acetic anhydride to 160° it forms an octacetyl ester, $C_{12}H_{14}O_3(O.C_2H_3O)_8$. It therefore contains eight hydroxyls. When hydrolyzed it yields d-glucose and d-fructose (lævogyratory). From the above facts we may infer that saccharose is derived from the two hexoses named, united through the aldehyde and ketone groups, a constitution which may be represented by the formulæ:



Lactose and maltose both cause reduction and yield osazones. On hydrolysis the former yields d-glucose and galactose, and the latter only d-glucose. They each consequently retain an aldehyde (or ketone) group, and their constitution may probably be represented thus:



The disaccharides are hydrolyzed by boiling with very dilute acids, or even with water, and by several enzymes such as diastase, emulsin, invertin, ptyalin, trypsin and pepsin.

Saccharose—Cane Sugar—exists in many roots, fruits and grasses, and is produced from the sugar-cane, *Saccharum officinarum*, sorghum, *Sorghum saccharatum*, beet, *Beta vulgaris*, and sugar-maple, *Acer saccharinum*.

For the extraction of sugar the expressed juice is heated in large pans to about 100° ; milk of lime is added, which causes the precipitation of albumin, wax, calcic phosphate, etc.; the clear liquid is drawn off, and "delimed" by passing a current of CO_2 through it; the clear liquid is again drawn off and evaporated, during agitation, to the crystallizing point; the product is drained, leaving what is termed **raw** or **muscovado sugar**, while the liquor which drains off is **molasses**. The sugar so obtained is purified by the process of "refining," which consists essentially in adding to the raw sugar, in solution, albumin in some form, which is then coagulated; filtering first through canvas, afterward through animal charcoal; and evaporating the clear liquid in "vacuum-pans," at a temperature not exceeding 72° , to the crystallizing point. The product is allowed to crystallize in earthen moulds; a saturated solution of pure sugar is poured upon the crystalline mass in order to displace the uncrystallizable sugar which still remains, and the loaf is finally dried in an oven. The liquid displaced as above is what is known as **sugar-house syrup**.

Pure sugar should be entirely soluble in water; the solution should not turn brown when warmed with dilute potassium hydroxide solu-

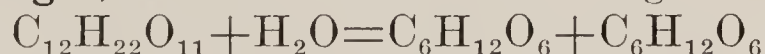
tion; should not reduce Fehling's solution, and should give no precipitate with ammonium oxalate.

Beet-sugar is the same as cane-sugar, except that, as usually met with in commerce, it is lighter, bulk for bulk. **Sugar-candy**, or **rock-candy**, is cane-sugar allowed to crystallize slowly from a concentrated solution, without agitation. **Maple-sugar** is a partially refined, but not decolorized variety of cane-sugar.

Saccharose crystallizes in small, white, monoclinic prisms; or, as sugar-candy, in large, yellowish, transparent crystals; sp. gr. 1.606. It is very soluble in water, dissolving in about one-third its weight of cold water, and more abundantly in hot water. It is insoluble in absolute alcohol or ether, and its solubility in water is progressively diminished by the addition of alcohol. Aqueous solutions of cane-sugar are dextrogyrous, $[\alpha]_D = +66.5^\circ$.

When saccharose is heated to 160° it fuses, and the liquid, on cooling, solidifies to a yellow, transparent, amorphous mass, known as **barley-sugar**; at a slightly higher temperature, it is decomposed into glucose and lævulosan; at a still higher temperature, H_2O is given off, and the glucose already formed is converted into glucosan; at about 200° the evolution of H_2O is more abundant, and there remains a brown material known as **caramel**, or **burnt sugar**; a tasteless substance, insoluble in strong alcohol, but soluble in H_2O , or in aqueous alcohol, and used to communicate color to spirits; finally, at higher temperatures, methyl hydride and the two oxides of carbon are given off; a brown oil, acetone, acetic acid, and aldehyde distil over; and a carbonaceous residue remains.

If saccharose is boiled for some time with H_2O , it is converted into **inverted sugar**, which is a mixture of glucose and fructose:



With a solution of saccharose the polarization is dextrogyrous, but, after inversion, it becomes lævogyrous, because the left-handed action of the molecule of fructose produced, $[\alpha]_D = -71.4^\circ$, is only partly neutralized by the right-handed action of the glucose, $[\alpha]_D = +52.6^\circ$. This inversion of cane sugar is utilized in the testing of samples of sugar. On the other hand, it is to avoid its occurrence, and the consequent loss of sugar, that the vacuum-pan is used in refining—its object being to remove the H_2O at a low temperature.

With potassium chlorate, sugar forms a mixture which detonates when subjected to shock, and which deflagrates when moistened with H_2SO_4 . Concentrated H_2SO_4 blackens it. Dilute HNO_3 , when heated with saccharose, oxidizes it to saccharic and oxalic acids.

When moderately heated with liquor potassæ, cane-sugar does not turn brown, as does glucose; but by long ebullition it is decomposed by the alkalies, much less readily than glucose, with formation of acids of the fatty series and oxalic acid.

With the bases, saccharose forms definite compounds called suc-

rates (improperly saccharates, a name belonging to the salts of saccharic acid). With Ca it forms five compounds. Calcium hydroxide dissolves readily in solutions of sugar, with formation of a Ca compound, soluble in H_2O , containing an excess of sugar.

During the process of digestion, probably in the small intestine, cane-sugar is inverted.

Lactose—Milk Sugar—Saccharum lactis (U. S. P.)—occurs in the milk of the mammalia, in the amniotic fluid of cows, and in the urine of women towards the end of gestation and during lactation. It may be obtained from skim-milk by coagulating the casein with a small quantity of H_2SO_4 , filtering, evaporating, redissolving, decolorizing with animal charcoal, and recrystallizing.

It forms prismatic crystals; sp. gr. 1.53; hard, transparent, faintly sweet, soluble in 6 parts of cold and 2.5 parts of boiling H_2O ; soluble in acetic acid; insoluble in alcohol and in ether. Its solutions are dextrogyrous $[\alpha]_{\text{D}} = +52.5^\circ$. The crystals, dried at 100° , contain 1Aq, which they lose at 150° .

Lactose is not altered by contact with air. Heated with dilute mineral acids or with strong organic acids, it is converted into galactose. HNO_3 oxidizes it to mucic and oxalic acids. A mixture of HNO_3 and H_2SO_4 converts it into an explosive nitro-compound. With organic acids it forms esters. With soda, potash and lime it forms compounds similar to those of saccharose, from which lactose may be recovered by neutralization, unless they have been heated to 100° , at which temperature they are decomposed. It reduces Fehling's solution, and reacts with Trommer's test. Its osazone fuses at 200° .

In the presence of yeast, lactose is capable of alcoholic fermentation, which takes place slowly, and, as it appears, without previous transformation of the lactose into glucose and galactose. On contact with putrefying proteins it enters into lactic fermentation. It is converted into galactose by the pancreatic secretion.

Maltose—is formed, along with dextrins, during the conversion of starch, or of glycogen, into sugar by the action of diastase (in malting grain), and of the enzymes of the saliva and the pancreatic juice. It is also an intermediate product in the hydrolysis of starch by dilute sulphuric acid. Maltose crystallizes in hard, white needles aggregated into crusts. It is less soluble in alcohol than is glucose, and has a much higher dextrogyratory power $[\alpha]_{\text{D}} = +137^\circ$. It reduces Fehling's solution. It is hydrolyzed by boiling with dilute acids, yielding only d-glucose. It is fermentable. Its osazone fuses at 206° . Nitric acid oxidizes it to d-saccharic acid.

Isomaltose—Gallisin—is formed along with maltose, in the action of diastase, saliva, or pancreatic juice, or of boiling dilute acids, on starch, and exists in beer and artificial glucose. It is also formed by the prolonged action of strong HCl on d-glucose. It is very soluble in water, very sweet,

and does not ferment, or does so very slowly. Its osazone forms yellow needles, which fuse at 150° , and are rather soluble in hot water.

TRISACCHARIDES.

Several members of this group have been obtained from different vegetables. They have the formula $C_{18}H_{32}O_{16}$. The best known are **Raffinose**, or **Melitose**, which occurs in eucalyptus-manna, in cotton seed, and in beet-sugar molasses; and **Melecitose**, from the manna of *Pinus larix*.

POLYSACCHARIDES.

The starches, gums, and celluloses, which form this class, have the empirical formula $C_6H_{10}O_5$, but their molecular weights are much greater than that represented by that formula. They are very widely distributed in vegetable nature. On hydrolysis they are finally decomposed to monosaccharides, for the most part hexoses, although some of the gums yield pentoses.

Starch—Amylum—the most important member of the group, exists in the roots, stems, and seeds of all plants; and is obtained commercially from rice, potatoes, and maize. It is a white powder, consisting of granules which are round, ovoid or irregular in outline, and, in some cases, marked with a central spot or line, called the **hilum**, and with concentric rings. Differences in the shape, size and markings of the granules are utilized to identify the vegetable from which the starch was obtained. Air-dried starch contains 18% of water, of which it loses 8% in vacuo, and the remainder only at 145° . Starch is insoluble in cold water and in alcohol. If 15 to 20 parts of H_2O are gradually heated with one part of starch, the granules swell at about 55° , and at 80° they have lost their structure, have swelled to thirty times their original volume, and have formed a homogeneous, translucent, gelatinous mass, commonly known as **starch paste**. This **hydrated starch** consists of an insoluble portion, **starch cellulose**, and a soluble portion, **granulose**, or **soluble starch**. Granulose forms an opalescent solution in water, from which it is precipitated as a white powder by alcohol. Its solutions are strongly dextrogyrous, $[\alpha]_D = +207^{\circ}$ (about). By prolonged boiling with water, or, more rapidly, by boiling dilute mineral acids, or by the action of diastatic enzymes, soluble starch is converted into dextrins, maltose, and finally, d-glucose. Dry heat causes the starch granules to burst, with formation of dextrin. A dilute solution of iodine produces a violet-blue color with starch, whether dry, hydrated, or in solution. The color is discharged by heat, but reappears on cooling. Concentrated HNO_3 dissolves starch in the cold, forming a nitro-product, called **xylodin**, or **pyroxam**, which is insoluble in water, soluble in a mixture of alcohol and ether, and explosive.

Glycogen—Animal Starch—occurs in the liver, the placenta, white blood corpuscles, pus cells, young cartilage cells, muscular tissue and many embryonic tissues, also in many molluscs. It is

best obtained from liver tissue, by extraction with hot water and precipitation by alcohol, after separation of protein bodies by potassium iodhydrargyrate and acetic acid. It is a snow-white, floury powder, amorphous, tasteless, and colorless; soluble in water, forming an opalescent solution, insoluble in alcohol or ether. Its solutions are strongly dextrogyrous, $[\alpha]_D = +196.6^\circ$. Glycogen is converted into dextrins, maltose, and, ultimately, d-glucose by the action of boiling dilute acids, and by the salivary, pancreatic and hepatic diastatic enzymes. Glycogen is colored wine-red by iodine, the color being discharged by heat and returning on cooling. Its solutions dissolve, but do not reduce cupric hydroxide.

Other starches are: **Paramylum**, occurring in certain infusoria; **Lichenin**, in lichens and mosses; and **Inulin**, in the roots of dahlia, chicory and other plants.

Gums—are amorphous, translucent substances occurring in many plants. They are insoluble in alcohol and in ether. With water some of them, the **true gums**, form clear solutions; while others, the **vegetable mucilages**, swell up to sticky masses which cannot be filtered through paper. On boiling with dilute H_2SO_4 the gums yield d-glucose, galactose, or l-arabinose. Nitric acid oxidizes them to mucic, oxalic and saccharic acids.

The commoner members of the group are: **Arabin**, the chief constituent of gum arabic (acacia) and gum senegal; and **Bassorin**, the chief ingredient of gum tragacanth, Bassora gum, and plum and cherry gums.

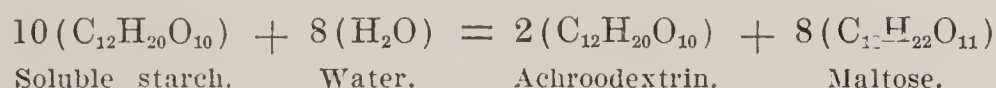
Dextrin—*British gum*—a substance resembling gum arabic in appearance and in many properties, is obtained by one of three methods: (1) by subjecting starch to a dry heat of 175° ; (2) by heating starch with dilute H_2SO_4 to 90° until a drop of the liquid gives only a wine-red color with iodine; neutralizing with chalk, filtering, concentrating, precipitating with alcohol; (3) by the action of diastase (infusion of malt) upon hydrated starch. As soon as the starch is dissolved the liquid must be rapidly heated to boiling to prevent saccharification.

Commercial dextrin is a colorless, or yellowish, amorphous powder, soluble in H_2O in all proportions, forming mucilaginous liquids. When obtained by evaporation of its solution, it forms masses resembling gum arabic in appearance. Its solutions are dextrogyrous, and reduce cupro-potassic solutions under the influence of heat, to amounts varying with the method of formation of the sample. It is colored wine-red by iodine. It is extensively used as a substitute for gum acacia.

By the action of diastase upon starch, four dextrins are produced: (1) **Erythrodextrin**, which is colored red by iodine, and which is easily attacked by diastase; (2) **Achroodextrin** α , not colored by iodine; partially converted into sugar by diastase; rotary power

$[a]_D = +210^\circ$; reducing power (glucose=100)=12; (3) **Achroodextrin β** , not colored by iodine, nor decomposable in twenty-four hours by diastase; rotary power $+190^\circ$; reducing power=12; (4) **Achroodextrin γ** , not colored by iodine, nor decomposed by diastase; slowly converted into glucose by dilute H_2SO_4 ; rotary power $=+150^\circ$; reducing power=28.

An explanation of this series of transformations has been suggested in the supposition that the molecule of starch consists of $50(C_{12}H_{20}O_{10})$; that this is first converted into soluble starch $10(C_{12}H_{20}O_{10})$; and that this is then converted into the different forms of dextrin by a series of hydrations attended by simultaneous formation of maltose, of which the final result might be represented by the equation:



Cellulose—Cellulin—Lignin—forms the basis of all vegetable tissues. It exists, almost pure, in the pith of elder and of other plants, in the purer, unsized papers, in cotton, and in the silky appendages of certain seeds. Cotton, freed from extraneous matter by boiling with KOH and afterwards with dilute HCl, yields pure cellulose (absorbent cotton). It is white, has the shape of the fiber from which it was derived, is insoluble in the usual solvents, but soluble in the dark blue liquid formed by dissolving copper in ammonia in contact with air.

Vegetable parchment—Parchment paper—is obtained by dipping unsized paper for an instant in H_2SO_4 , diluted with an equal volume of H_2O , washing thoroughly, and drying. It is a tough material resembling animal parchment.

Gun-cotton—Pyroxylin—Nitrocellulose—is obtained by dipping pure cotton in a cold mixture of one part of HNO_3 and two-thirds of H_2SO_4 for from three to ten minutes, washing thoroughly, and drying. It consists of hexanitrocellulose, $C_{12}H_{14}(O.NO_2)_6O_4$, is violently explosive, and is insoluble in a mixture of alcohol and ether.

Soluble pyroxylin—is obtained by acting on cotton with a warm mixture of twenty parts of nitre and thirty parts of concentrated H_2SO_4 , washing and drying. It consists of penta- and tetra-nitrocellulose, is soluble in a mixture of alcohol and ether, and is used in the preparation of collodion. **Explosive gelatin, or smokeless powder**, is a desiccated mixture of nitro-glycerol and collodion. **Celluloid** is a mixture of gun-cotton and camphor, combined by pressure.

Tests for Carbohydrates.—A. *Furfurole Reaction—Tollens' Reaction* for pentoses (not hexoses) depends upon the fact that these compounds yield furfurole by loss of water when they are heated with HCl. The reagent consists of 1 gm. phloroglucin, dissolved in 500 cc. of 30 per cent. HCl, to which 30 drops of a 30 per

cent. solution of FeCl_3 are added. About 5 cc. of the reagent are heated to boiling, and the liquid added. The formation of a cherry-red color indicates the presence of a pentose. Orcin may be substituted for phloroglucin in the reagent, when the color produced is green. Orcin has the advantage over phloroglucin that the glucuronates do not react with the former, but do with the latter.

B. *Aldehyde and Ketone Reactions*.—These reactions depend upon the presence in the carbohydrates of the CHO or CO group, and are consequently given by cane-sugar, non-reducing dextrans and starch, which do not contain such groups, only after their hydrolysis by boiling with dilute acids; but are given by other substances containing ketone or aldehyde groups.

1. *Copper Reduction Tests*.—These and other reduction tests are produced not only by aldoses and ketoses, but also by other reducing agents. Therefore, such substances, as well as albumin, must be excluded before these tests are resorted to. This may be accomplished by Focke's method, by boiling 10 cc. of liquid (urine) with 5 cc. of CuSO_4 solution (1:10), filtering, adding 2 cc. Na_2CO_3 solution (1:10) to the cool filtrate, and filtering again after standing.

Trommer's Reaction is the earliest form of reduction test for sugar. It consists in adding about one-eighth of NaOH or KOH solution (1:10) to the dilute saccharine liquid, then two to three drops of CuSO_4 solution (1:10) and heating the blue liquid just to boiling. A yellow ppt. is formed, which becomes darker and reddish on boiling.

Fehling's Test.—The reagent must be kept in two solutions, which are to be mixed immediately before use. If the reagent is made in a single solution it is prone to self-reduction. Solution I consists of 34.653 gms. of crystallized CuSO_4 , dissolved in water to 500 cc.; and II, of 130 gms. of Rochelle salt dissolved to 500 cc. in NaOH solution of sp. gr. 1.12. When required for use equal volumes of the two solutions are mixed, and the mixture diluted with four volumes of water. A few cc. of this liquid are heated to boiling, and the saccharine liquid (urine) added in small portions, the contents of the test-tube being heated short of boiling, but not boiled, after each addition. A reducing sugar produces a yellow or red ppt., which forms more or less rapidly according to the amount of sugar present. The liquid should not be boiled after addition of urine, as creatinine and uric acid may reduce by boiling. Glucuronates and glycosurates also reduce. There are many modifications of this test, in which potassium tartrate, mannite, glycerol, etc., are used in place of Rochelle salt, but they present no advantages over the above. *Pavy's solution* is a modified Fehling, containing a notable amount of ammonia. It has the advantage for quantitative work that the blue color is more sharply discharged on total reduction, but it is open to the objection that the ppt. is soluble in the ammoniacal liquid.

2. *Bismuth Reduction Tests.*—*Boettger's test* may be applied either in the manner originally indicated, or in *Nylander's* or *Almén's* modifications. Equal portions of the liquid are placed in two test tubes, to each of which enough solution of Na_2CO_3 is added to make the reaction distinctly alkaline, and to one a little powdered bismuth subnitrate, and to the other a little powdered litharge are added. The contents of the two tubes are then heated to boiling, when, if the bismuth powder becomes black and the litharge remains unchanged, the presence of a reducing sugar may be inferred. The purpose of the litharge is to guard against error from the presence of sulphur compounds, which blacken both the bismuth and lead powders. *Nylander's solution* is made by adding 4 gms. of Rochelle salts, 2 gms. of bismuth subnitrate and 10 gms. of caustic soda to 90 cc. of water, boiling, cooling and filtering. To use the test 1 cc. of the reagent is added to the liquid and the mixture boiled, when a reducing sugar causes the formation of a gray or black ppt. A parallel testing with litharge is also required. An affirmative result is obtained with urine in the absence of sugar when large doses of quinine have been taken, but uric acid and creatinine do not react, and therefore this reaction is preferable to the copper reduction tests, although glucuronates react with it.

3. *Osazone Reaction.*—The *phenylhydrazine test*, or *Fischer's*, or *Riegler's test* depends upon the formation of osazones by all monosaccharides and disaccharides containing CO or CHO groups. To 10 cc. of the liquid (urine) in a test tube, add 0.5 gm. phenylhydrazine hydrochloride and 1 gm. sodium acetate, and cause the powders to dissolve by warming, and, if necessary, the addition of water, and leave the test tube in a boiling-water bath for one hour, after which cool it by immersion in cold water. If a ketose or aldose, whether hexose or pentose, or a glucuronate is present a yellow ppt. is formed, usually crystalline, which should be collected and examined microscopically. Needle-shaped crystals are formed by glucose, fructose, maltose and glucuronic acid. The osazones of glucose and fructose are one and the same substance. The several osazones have different fusing points: that of glucuronic acid, 114° – 115° ; of isomaltose, 150° – 153° ; of arabinose, 159° ; of galactose, 193° ; of glucose and fructose, 204° – 205° , and of maltose, 206° . To determine the fusing point the ppt. is collected, dissolved in hot alcohol, the solution filtered and evaporated, the crystals dried over H_2SO_4 , placed in a small closed tube attached to the bulb of a thermometer by a pasted slip of paper, and heated in a paraffin bath, the temperature being noted when the material fuses. Aldehydes and ketones also form hydrazones.

4. *Fermentation Test.*—Three Smith's fermentation-tubes are used, one (A) completely filled with water, one (B) with a dilute solution of glucose, and the third (C) with the liquid (urine) to be

tested, and each containing a little compressed yeast. The three tubes are put in warm place and left over-night, when if gas has collected in B and C and none in A the urine contains sugar; if gas has collected in B, but none in A or C it is absent; under any other circumstances the yeast is at fault. The only substances other than glucose which respond to this test are the other fermentable carbohydrates, lactose, maltose and fructose.

CARBOXYLIC ACIDS.

These compounds are the third products of oxidation of the CH_3 groups of the paraffins and contain the characterizing group of atoms $\text{O}:\text{C}.\text{OH}$ (carboxyl). They are either pure acids, containing only the carboxyl and hydrocarbon groups; or alcohol-acids, containing also the groups CH_2OH , CHOH or COH ; or aldehyde-acids, containing CHO ; or ketone-acids, containing CO ; or of still more complex function, containing two or more of the above groups.

The most important of the pure acids are those of the acetic ($\text{C}_n\text{H}_{2n}\text{O}_2$), and oxalic ($\text{C}_n\text{H}_{2n-2}\text{O}_4$) series, the former of which are monobasic, the latter dibasic. Other pure acids of higher basicity are also known in which the carboxyl groups are substituted for hydrogen atoms in the hydrocarbon.

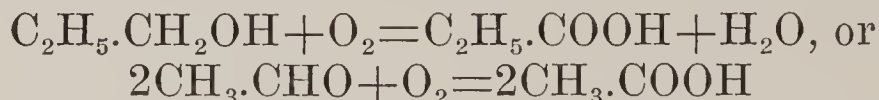
PARAFFIN MONOCARBOXYLIC ACIDS—VOLATILE FATTY ACIDS— ACETIC SERIES—SERIES $\text{C}_n\text{H}_{2n}\text{O}_2$

The lowest terms of the series are volatile liquids, the highest are solids and exist in their glycerol esters in the fats; hence the name of **volatile fatty acids**. The solid acids, the tenth and higher of the series, cannot be distilled without decomposition except in superheated steam.

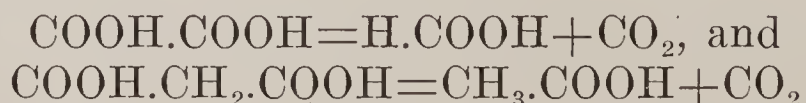
As the hydrocarbons may be considered as the hydrides of the alkyls, and the alcohols as their hydroxides, so the acids may be considered as the hydroxides of the **acidyls**: the acid or oxidized radicals. Thus acetic acid is acetyl hydroxide, $(\text{CH}_3.\text{CO})\text{OH}$.

These acids may be obtained:

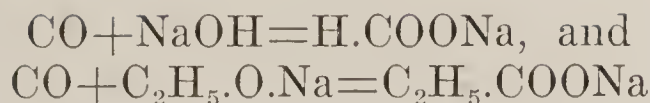
(1) By oxidation of the corresponding alcohol or aldehyde:



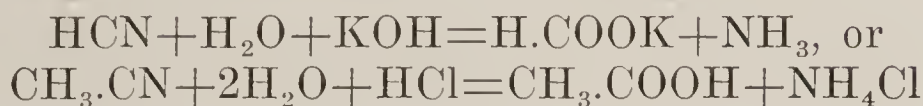
(2) By decomposition of the dicarboxylic acids, with elimination of carbon dioxide:



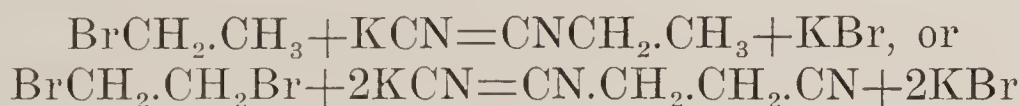
(3) By the action of carbon monoxide upon an alkaline hydroxide or alcoholate:



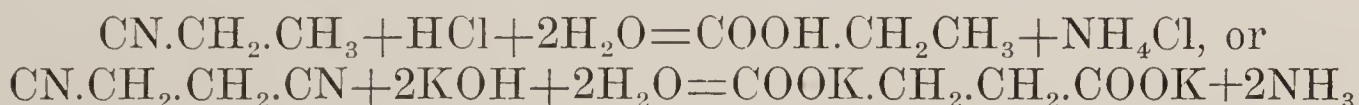
(4) From the nitriles, or hydrocyanic esters, by the action of acids or alkalies in the presence of water:



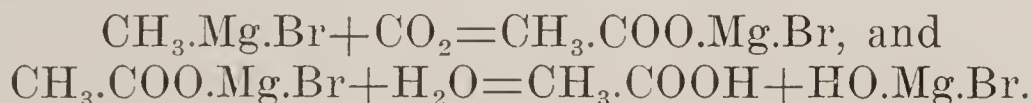
This constitutes a general method for the introduction of carboxyl, starting from the haloid derivatives of the hydrocarbon. This is converted into the cyanide, or nitrile by heating with alcoholic potassium cyanide:



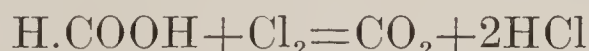
and the cyanide is then converted into the acid by elimination of the nitrogen as ammonia, and the substitution of OOH in its place by the action of acids or of alkalies:



(5) By passing carbon dioxide through ethereal solutions of alkyl magnesium bromides or iodides and hydrolyzing the product:



Methan Acid—Formic Acid—H.COOH.—Although it is the first term of this series, formic acid differs from its superior homologues in several respects: (1) It is not a pure acid, but an aldehyde-acid, the single carbon atom forming part of both groups: $\text{O}:\text{C}\begin{smallmatrix} \text{OH} \\ \diagdown \\ \text{H} \end{smallmatrix}$; (2) The halogens do not convert it into halide-formic (or carbonic) acids, but split it to carbon dioxide and the hydracid:



(3) By elimination of water it yields carbon monoxide:

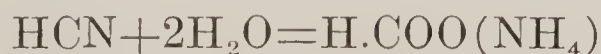


(4) It produces no acidyl halide or anhydride corresponding to those of its superior homologues.

It occurs in the bodies of ants and of other insects, and in the blood, bile, perspiration and muscular fluid of mammalia. It is produced by oxidation of sugar, starch, gelatin, albumin, etc.; in the fermentation of diabetic urine; by the action of potash upon chloroform:



By the action of hydrating agents upon its nitrile, hydrocyanic acid:



And by decomposition of oxalic acid in the presence of glycerol at about 100° :



It is a colorless liquid of acid taste and penetrating odor, b. p. 100° , crystallizes at 0° , miscible with water. It is decomposed by mineral acids to carbon monoxide and water: $\text{H.COOH} = \text{CO} + \text{H}_2\text{O}$; by oxidizing agents to carbon dioxide and water: $2\text{H.COOH} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{CO}_2$; and by caustic alkalies to a carbonate and hydrogen: $\text{H.COOH} + \text{KOH} = \text{KHCO}_3 + \text{H}_2$. It reduces the salts of Au, Ag, and Hg.

Orthoformic Acid, $\text{CH}(\text{OH})_3$, so called because of its analogy to tribasic or "ortho" phosphoric acid $\text{OP}(\text{OH})_3$ is only known in its esters (p. 277).

Ethan Acid—Acetic Acid—Acetyl Hydroxide—Acidum aceticum (U. S. P.)— CH_3COOH —is formed by the general methods, and (1) by the action of carbon dioxide on sodium methyl: $\text{CO}_2 + \text{NaCH}_3 = \text{CH}_3\text{COONa}$; and (2) by the oxidation of many organic substances: starch, sugar, gelatin, fibrin, cellulose, tartaric and citric acids, etc. Commercially it is obtained as acetic acid and as vinegar. As the former it is produced by the dry distillation of wood, in which four products are obtained: charcoal, remaining in the retort, an illuminating gas, a tarry liquid, wood-tar, and an acid liquid, "crude wood vinegar" or "pyroxylic spirit." The last is a highly complex liquid, containing acids of this series, methyl acetate, and cyclic compounds. It is redistilled fractionally, the first portions being used as a source of methylic alcohol, and the later portions of acetic acid. In these the acid is converted into sodium acetate, which, after calcination, is decomposed by H_2SO_4 , and the liberated acetic acid distilled off. The product so obtained, the commercial acid, contains 36 per cent. of true acetic acid, sp. gr. 1.047.

Vinegar is obtained by the indirect atmospheric oxidation of various alcoholic liquids, containing less than 10 per cent. of ethyl alcohol, under the influence of the growth of a true ferment, *Bacterium aceti*, or "mother of vinegar," with free access of air. It contains from 5 to 10 per cent. of acetic acid.

Pure acetic acid, called **glacial acetic acid** (**acidum aceticum glaciale**, U. S. P.), is obtained by distilling dry sodium acetate with a slight excess of H_2SO_4 . It is a colorless liquid, b. p. 119° , crystallizes to an ice-mass at 17° , sp. gr. 1.0497 at 20° , having an acid taste and the odor of vinegar, and causing vesication when applied to the skin. Glacial acetic acid on dilution with water contracts until the sp. gr. becomes 1.0754 with a dilution of 77 per cent. of acid, corresponding to a hydrate: $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$, and on further dilution the sp. gr. diminishes until at 50 per cent. it is the same as that of the glacial acid. Acetic acid is a good solvent for many organic sub-

stances, and is itself soluble in water and in alcohol in all proportions.

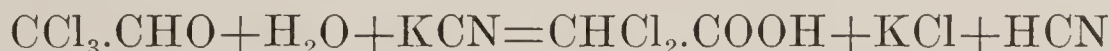
Vapor of acetic acid burns with a pale-blue flame and is decomposed at a red heat. Glacial acetic acid only decomposes calcium carbonate in the presence of water. Hot H_2SO_4 blackens and decomposes it, SO_2 and CO_2 being given off. Solutions of potassium acetate, when electrolyzed, yield ethane, C_2H_6 . Under ordinary circumstances chlorine acts upon acetic acid slowly, more actively under the influence of sunlight, to form the three products of substitution mentioned below.

Acetates are soluble in water, except basic ferric acetate. Potassium acetate, heated with arsenic trioxide forms cacodyl oxide. Calcium acetate, when heated alone, yields acetone; and with calcium formate, aldehyde.

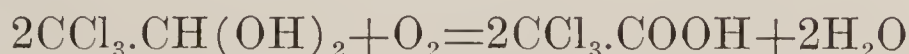
Monochloracetic acid is a solid, f. p. 62° , b. p. 186° , obtained, along with acetyl chloride, by the action of chlorine upon acetic anhydride:



Dichloracetic acid is a colorless liquid, b. p. 190° , obtained by heating chloral with aqueous potassium cyanide:



Trichloracetic acid is an odorless, strongly vesicant, crystalline solid, f. p. 46° , b. p. 195° , obtained by oxidation of chloral hydrate by nitric acid:



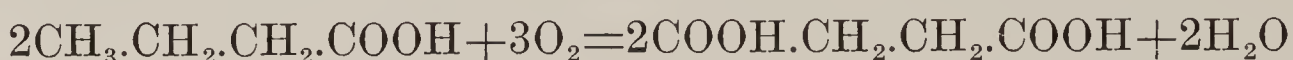
Propan Acid—Propionic Acid—Methylacetic acid— $\text{CH}_3.\text{CH}_2.\text{COOH}$ —is formed by the action of caustic potash upon sugar, starch and gum; during acetic fermentation; in the distillation of wood; during the putrefaction of peas, beans, etc.; by the oxidation of normal propylic alcohol, etc. It is best prepared by heating ethyl cyanide with potash until the odor of the ester has disappeared; the acid is then liberated from its potassium compound by H_2SO_4 and purified.

It is a colorless liquid, sp. gr. 0.996, b. p. 140° , solidifies at -36.5° , odor and taste like those of acetic acid, mixes with water and alcohol. Its salts are crystalline and soluble.

Butan Acid—Butyric Acid—Ethylacetic Acid— $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{COOH}$ —exists in milk, perspiration, muscle, spleen, contents of stomach and large intestine, feces, and guano; in butter, particularly when rancid; in certain fruits and in yeast. It is formed by the action of H_2SO_4 and manganese dioxide, aided by heat, upon cheese, starch, gelatin, etc.; during the combustion of tobacco (as ammonium butyrate); by the action of HNO_3 upon oleic acid during the decomposition of many animal and vegetable substances, and particularly by *butyric fermentation* of carbohydrates in presence of

proteins. This fermentation occurs in two stages: First the glucose is converted into lactic acid: $C_6H_{12}O_6 = 2C_3H_6O_3$; and this in turn is decomposed into butyric acid, carbon dioxide, and hydrogen: $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$.

Butyric acid is a colorless, mobile liquid, having a disagreeable, persistent odor of rancid butter, and a sharp, acid taste; soluble in water, alcohol, ether, and methyl alcohol; boils at 164° , distilling unchanged; solidifies in a mixture of solid carbon dioxide and ether; sp. gr. 0.974 at 15° ; a good solvent of fats. It is not acted on by cold H_2SO_4 or HNO_3 . Hot HNO_3 oxidizes it to succinic acid:



Dry Cl in sunlight, and Br under heat and pressure form several products of substitution. The butyrates are soluble in water.

Butyric acid is formed in the intestine, by the process of fermentation mentioned above, at the expense of those portions of the carbohydrate elements of food which escape absorption, and is discharged with the feces as ammonium butyrate.

Isobutyric Acid—Dimethylacetic acid— $\begin{matrix} CH_3 \\ \diagup \\ CH \\ \diagdown \\ CH_3 \end{matrix} .COOH$ —boils at 155° , has been found in human feces. It corresponds to isobutyl alcohol, from which it is produced by oxidation.

Pentan Acids—Valerianic Acids—Valeric Acids— $C_4H_9.COOH$ —102.—Corresponding to the four primary amylic alcohols, there are four possible amylic or valerianic acids:

Normal Valerianic Acid—Valeric Acid—Propyl-acetic acid—is obtained by the oxidation of normal amylic alcohol. It is an oily liquid, boils at 185° , and has an odor resembling that of butyric acid.

Ordinary Valerianic Acid—Valeric Acid—Isopropyl-acetic acid—Isovaleric acid—This acid exists in the oil of the porpoise, and in valerian root and in angelica root. It is formed during putrid fermentation or oxidation of proteins. It occurs in the urine and feces in typhoid, variola, and acute atrophy of the liver. It is also formed in a variety of chemical reactions, and notably by the oxidation of amylic alcohol.

The ordinary valerianic acid is an oily, colorless liquid, having an odor of old cheese, and a sharp, acrid taste. It solidifies at -51° ; boils at 173° – 175° ; sp. gr. 0.9343–0.9465 at 20° ; burns with a white, smoky flame. It dissolves in 30 parts of water, and in alcohol and ether in all proportions. It dissolves phosphorus, camphor and certain resins.

Hexan Acids—Caproic Acids—Hexylic acids— $C_5H_{11}.COOH$ —116.—There exist seven isomeres having the composition indicated above, some of which have been prepared from butter, cocoa-oil and cheese, and by decomposition of amyl cyanide, or by oxidation of hexyl alcohol.

The acid obtained from butter, in which it exists as a glyceric ester, is a colorless, oily liquid, boils at 205° ; sp. gr. 0.931 at 15° , has an odor of perspira-

tion and a sharp, acid taste; is very sparingly soluble in water, but soluble in alcohol. It is the normal hexylic acid: $\text{CH}_3(\text{CH}_2)_4\text{COOH}$.

Caprylic Acid—*Octylic acid*— $\text{C}_7\text{H}_{15}\text{COOH}$ —144—accompanies caproic acid in butter, cocoa-oil, etc. It is a solid; fuses at 15° ; boils at 236° ; almost insoluble in H_2O .

Capric Acid—*Decylic acid*— $\text{C}_9\text{H}_{19}\text{COOH}$ —172—exists in butter, cocoa-oil, etc., associated with caproic and caprylic acids in their glyceric esters, and in the residues of distillation of Scotch whisky, as amyl caprate. It is a white, crystalline solid; melts at 27.5° ; boils at 273° .

Lauric Acid—*Laurostearic acid*— $\text{C}_{11}\text{H}_{23}\text{COOH}$ —200—is a solid, fusible at 43.5° ; obtained from laurel berries, cocoa-butter and other vegetable fats.

Myristic Acid— $\text{C}_{13}\text{H}_{27}\text{COOH}$ —228.—A crystalline solid, fusible at 54° ; existing in many vegetable oils, cow's butter and spermaceti.

Palmitic Acid— $\text{C}_{15}\text{H}_{31}\text{COOH}$ —256—exists in palm-oil, in combination when the oil is fresh, and free when the oil is old; it also enters into the composition of nearly all animal and vegetable fats. It is obtained from the fats, palm-oil, etc., by saponification with caustic potash and subsequent decomposition of the soap by a strong acid. It is formed by the action of caustic potash in fusion upon cetyl alcohol (ethal), and by the action of the same reagent upon oleic acid.

Palmitic acid is a white, crystalline solid; odorless, tasteless; lighter than H_2O , in which it is insoluble; quite soluble in alcohol and in ether; fuses at 62° ; distils unchanged with vapor of water.

Margaric Acid— $\text{C}_{16}\text{H}_{33}\text{COOH}$ —270—formerly supposed to exist as a glyceride in all fats, solid and liquid. What had been taken for margaric acid was a mixture of 90 per cent. of palmitic and 10 per cent. of stearic acid. It is obtained by the action of potassium hydroxide upon cetyl cyanide, as a white, crystalline body; fusible at 59.9° .

Stearic Acid— $\text{C}_{17}\text{H}_{35}\text{COOH}$ —284—exists as a glyceride in all solid fats and in many oils, and also free to a limited extent.

To obtain it pure the fat is saponified with an alkali, and the soap decomposed by HCl ; the mixture of fatty acids is dissolved in a large quantity of alcohol, and the boiling solution *partly* precipitated by the addition of concentrated solution of barium acetate. The precipitate is collected, washed and decomposed by HCl ; the stearic acid which separates is washed and recrystallized from alcohol. The process is repeated until the product fuses at 70° . Stearic acid is formed from oleic acid by the action of iodine under pressure at 270° – 280° .

Pure stearic acid is a colorless, odorless, tasteless solid; fusible at 70° ; unctuous to the touch; insoluble in H_2O , very soluble in alcohol and in ether. The alkaline stearates are soluble in H_2O ; those of Ca, Ba, and Pb are insoluble.

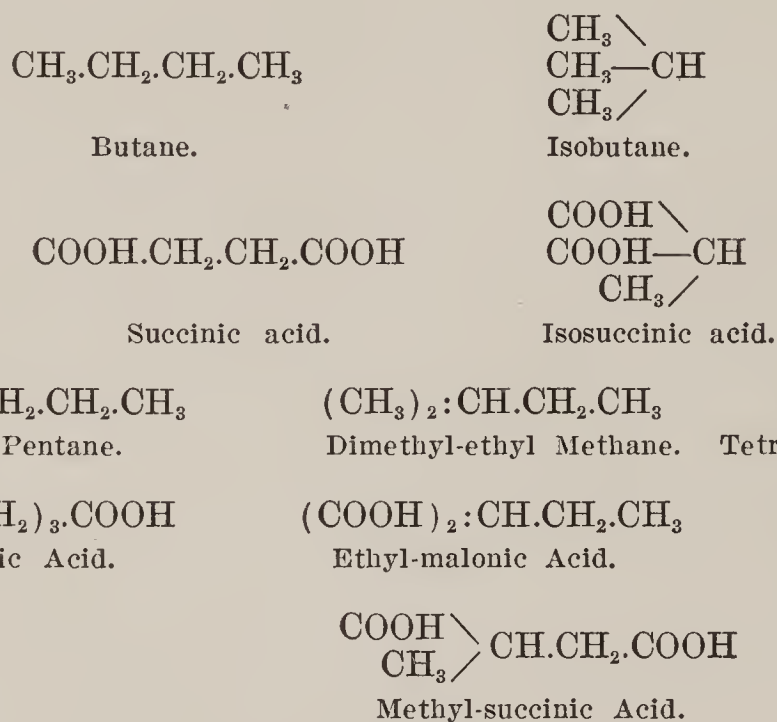
Stearic and palmitic acids exist free in the intestine during the digestion of fats, a portion of which is decomposed by the action

of the pancreatic secretion into fatty acids and glycerol. The same decomposition also occurs in the presence of putrefying proteins.

Arachic Acid— $C_{19}H_{39}.COOH$ —312—exists as a glyceride in peanut oil (now largely used as a substitute for olive oil), in oil of ben, and in small quantity in butter. It is a crystalline solid, which melts at 75° .

PARAFFIN DICARBOXYLIC ACIDS—OXALIC SERIES— $C_nH_{2n-2}O_4$

These acids are derivable from the paraffins by oxidation of two CH_3 groups, or from the diprimary alcohols by oxidation of the CH_2OH groups. They contain two carboxyl groups and are therefore dibasic. But one acid is possibly derivable from ethane (oxalic acid), and from propane (malonic acid). From the two butanes two acids are derivable; from the three pentanes four acids, and from the five hexanes nine acids; all of which are known. The molecular structure of the acids derivable from the butanes and pentanes is shown in the following formulæ:



As the monocarboxylic acids may be considered as the hydroxides of the *acidyls* (p. 250), corresponding to the *alkyls* of the monohydric alcohols (p. 211), so the dicarboxylic acids are the hydroxides of bivalent acid radicals, which we will call **acidylenes**, corresponding to the *alkylenes* of the dihydric alcohols (p. 221).

The acids of this series may be obtained: (1) By the oxidation of the corresponding diprimary alcohols, dialdehydes, primary oxyaldehydes, primary oxyacids, aldehyde acids, paraffin monocarboxylic acids, olefine monocarboxylic acids or paraffins.

(2) By the reduction of the olefine dicarboxylic acids.

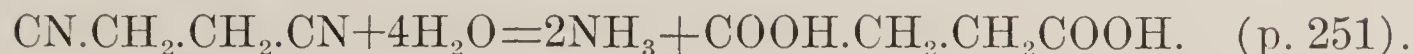
(3) By the action of silver upon the moniodo or monobromo fatty acids:



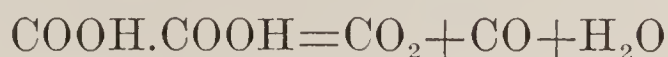
(4) By the action of acids or alkalies upon the cyano fatty acids:



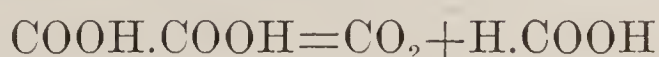
or upon the dicyanides:



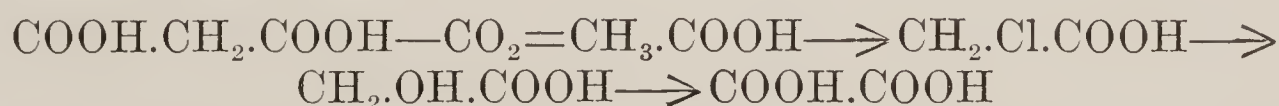
The action of heat upon these acids and their salts differs according to the attachment of the carboxyl groups. (1) Oxalic acid and acids in which the two carboxyls are attached to the same carbon atom are either decomposed into the two oxides of carbon and water:



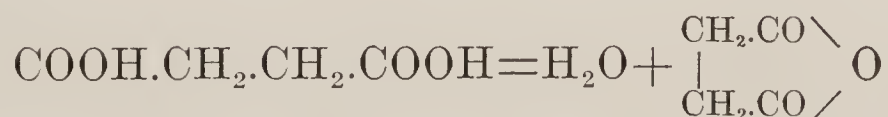
or into carbon dioxide and a fatty acid:



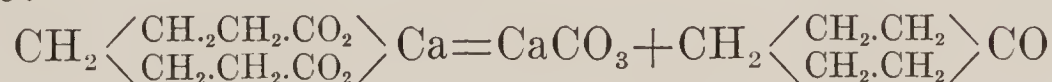
This splitting off of CO_2 occurs more readily with other acids than with the monocarboxylic acids (p. 251), and may be utilized in the same manner to pass to compounds of less carbon content. Thus from malonic acid to acetic acid, to monochloroacetic acid, to glycollic acid and to oxalic acid:



(2) When the two carboxyls are attached to neighboring carbon atoms the acids are decomposed into water and an anhydride (p. 269):



(3) When the carboxyls are attached to remote carbon atoms their calcium salts are converted by heat into cyclic ketones and carbonate:



Oxalic Acid— $\text{COOH}.\text{COOH}$ —90— $\text{C}_2\text{H}_2\text{O}_4$, 2Aq—126—does not occur free in nature, but in the oxalates of K, Na, Ca, Mg, and Fe in the juices of many plants: sorrel, rhubarb, cinchona, oak, etc.; as a native ferrous oxalate; and in small quantity in human urine. It is prepared artificially by oxidizing sugar or starch by HNO_3 , or by the action of an alkaline hydroxide in fusion upon sawdust. The soluble alkaline oxalate obtained by the latter method is converted into the insoluble Ca or Pb salt, which is washed and decomposed by an equivalent quantity of H_2SO_4 or H_2S ; and the liberated acid purified by recrystallization.

Oxalic acid is also formed by the oxidation of many organic substances: alcohol, glycol, sugar, etc.; by the action of potash in fusion upon the alkaline formates; and by the action of K or Na upon CO_2 .

It crystallizes in transparent prisms, containing 2 Aq, which effloresce on exposure to air, and lose their Aq slowly but completely at 100° , or in a dry vacuum. It fuses at 98° in its Aq; at $110\text{--}132^{\circ}$ it sublimes in the anhydrous form, while a portion is decomposed; above 160° the decomposition is more extensive; H_2O , CO_2 , CO , and formic acid are produced, while a portion of the acid is sublimed unchanged. It dissolves in 15.5 parts of water at 10° ; the presence of HNO_3 increases its solubility. It is quite soluble in alcohol. It has a sharp taste and an acid reaction in solution.

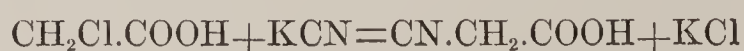
Oxalic acid is readily oxidized; in watery solution it is converted into CO_2 and H_2O , slowly by simple exposure to air, more rapidly in the presence of platinum-black or of the salts of platinum and gold, under the influence of sunlight, or when heated with HNO_3 , manganese dioxide, chromic acid, Br , Cl , or hypochlorous acid. Its oxidation, when it is triturated dry with lead dioxide, is sufficiently active to heat the mass to redness. H_2SO_4 , H_3PO_4 and other dehydrating agents decompose it into H_2O , CO and CO_2 .

Analytical Characters.—(1) In neutral or alkaline solution: a white ppt. with a solution of Ca salt. (2) Silver nitrate: a white ppt., soluble in HNO_3 , and in NH_4OH . The ppt. does not darken when the fluid is boiled, but when dried and heated on platinum foil, it explodes. (3) Lead acetate, in solutions not too dilute: a white ppt., soluble in HNO_3 , insoluble in acetic acid.

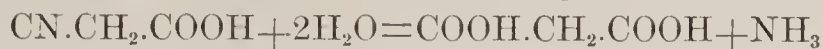
Toxicology.—Although certain oxalates are constant constituents of vegetable food and of the human body, the acid itself, as well as monopotassic oxalate, is a violent poison when taken internally, acting both locally as a corrosive upon the tissues with which it comes in contact and as a true poison, the predominance of either action depending upon the concentration of the solution. Dilute solutions may produce death without pain or vomiting, and after symptoms resembling those of narcotic poisoning. Death has followed a dose of 4 gm. of the solid acid, and recovery a dose of 30 gm. in solution. When death occurs, it may be almost instantaneously, usually within half an hour; sometimes after weeks or months, from secondary causes.

The *treatment*, which must be as expeditious as possible, consists in the administration, *first*, of lime or magnesia, or a soluble salt of Ca or Mg, suspended or dissolved in a *small* quantity of H_2O or mucilaginous fluid; afterward, if vomiting has not occurred spontaneously, and if the symptoms of corrosion have not been severe, an emetic may be given. The alkaline carbonates are of no value in cases of oxalic-acid poisoning, as the oxalates which they form are soluble and almost as poisonous as the acid itself. The ingestion of water, or the administration of warm water as an emetic, is contraindicated when the poison has been taken in the solid form (or where doubt exists as to what form it was taken in), as they dissolve, and thus favor the absorption of the poison.

Malonic Acid— $\text{CH}_2\begin{smallmatrix} \diagup \text{COOH} \\ \diagdown \text{COOH} \end{smallmatrix}$ —is a product of the oxidation of malic acid or of normal propyl glycol. It is best obtained by the general method 4, p. 257. Monochloroacetic acid is converted into cyano-acetic acid by heating in alkaline solution with KCN:



The cyano-acid is then hydrolyzed by heating with KOH or HCl, thus:



It forms large prismatic crystals, soluble in water, alcohol and ether; fusible at 132° , and decomposed at about 150° into acetic acid and carbon dioxide.

Succinic Acid— $\begin{array}{c} \text{CH}_2-\text{COOH} \\ | \\ \text{CH}_2-\text{COOH} \end{array}$ —118—exists in amber, coal, fossil wood, and

in small quantity in animal and vegetable tissues. Its presence has been detected in the normal urine after the use of fruits and of asparagus, in the parenchymatous fluids of the spleen, thyroid, and thymus, and in the fluids of hydrocele and of hydatid cysts. It is also formed in small quantity during alcoholic fermentation; as a product of oxidation of many fats and fatty acids; and by synthesis from ethylene cyanide:



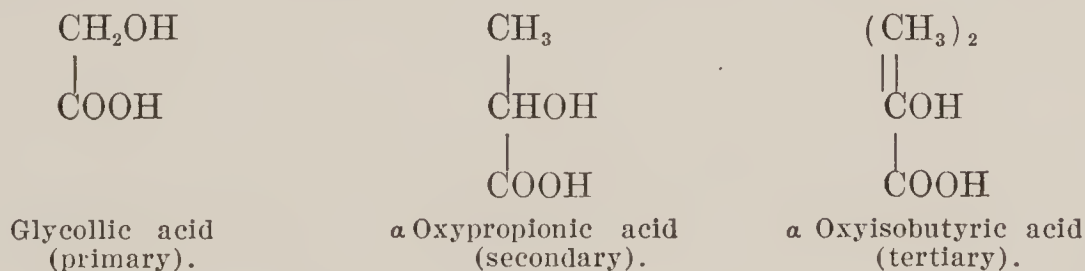
It may also be obtained by dry distillation of amber, or by the fermentation of malic acid.

It crystallizes in large prisms or hexagonal plates, which are colorless, odorless, permanent in air, acid in taste, soluble in water, sparingly so in ether and in cold alcohol. It fuses at 180° , and distils with partial decomposition at 235° . It withstands the action of oxidizing agents. Reducing agents convert it into the corresponding acid of the fatty series, butyric acid. With Br it forms products of substitution. H_2SO_4 is without action upon it. Phosphoric anhydrides remove H_2O and convert it into **succinic anhydride**, $\text{C}_4\text{H}_4\text{O}_3$.

Glutaric Acid— $\text{COOH} \cdot (\text{CH}_2)_3 \cdot \text{COOH}$ —*Normal Pyrotartaric acid*—the next superior homologue of succinic acid, is formed by reduction of α oxyglutaric acid (p. 263). It crystallizes in large plates, very soluble in water, which fuse at 27° . The corresponding amido-acid is one of the products of decomposition of protein bodies.

ALCOHOL-ACIDS—OXYACIDS.

These acids contain, besides the carboxyl group, one of the groups CH_2OH , CHOH , or COH , which characterize the primary, secondary, and tertiary alcohols. They, therefore, have the function of alcohols, primary, secondary, or tertiary, as well as that of acids:



They may be considered as derived either from the di- and poly-atomic alcohols (glycols, glycerols, etc.) by incomplete oxidation, as $\text{COOH} \cdot \text{CH}_2\text{OH}$ from $\text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}$; or from the pure acids by substitution of OH for H atoms in the remaining hydrocarbon groups, as $\text{CH}_2\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$; $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2 \cdot \text{COOH}$, and $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH}$ from $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

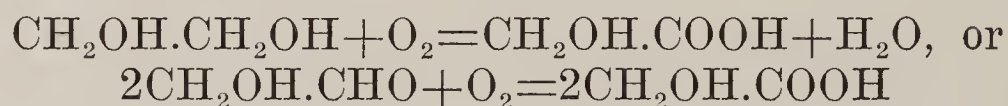
The *basicity* of these acids is represented by the number of carboxyl groups which they contain, their *atomicity* by the number of hydroxyls. Thus $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{COOH}$ is monobasic and triatomic.

The algebraic formulæ of the several monobasic series are $C_nH_{2n}O_3$; $C_nH_{2n}O_4$, $C_nH_{2n}O_5$, etc., those of the dibasic series $C_nH_{2n-2}O_5$, $C_nH_{2n-2}O_6$, etc.; and those of the tribasic series $C_nH_{2n-4}O_7$, $C_nH_{2n-4}O_8$, etc.

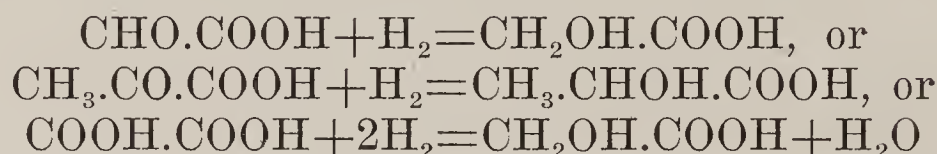
OXYACETIC SERIES. $C_nH_{2n}O_3$

The acids of this series contain one carboxyl and one alcoholic group. They are, therefore, monobasic and diatomic, and may be considered as derived from the glycols by oxidation of one CH_2OH group, or from the acids of the acetic series by substitution of OH for H in a hydrocarbon group (oxyacetic).

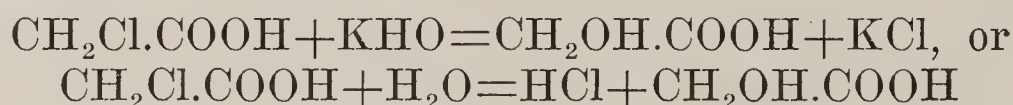
They are formed: (1) By the limited oxidation of the corresponding glycols or oxyaldehydes:



(2) By the action of nascent hydrogen upon the aldehyde or ketone acids, or upon the acids of the oxalic series:



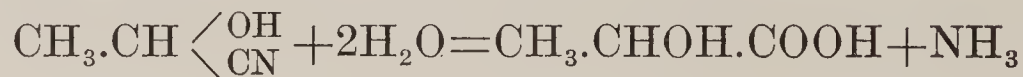
(3) By heating the monohalogen fatty acids with silver or potassium hydroxides, or with water:



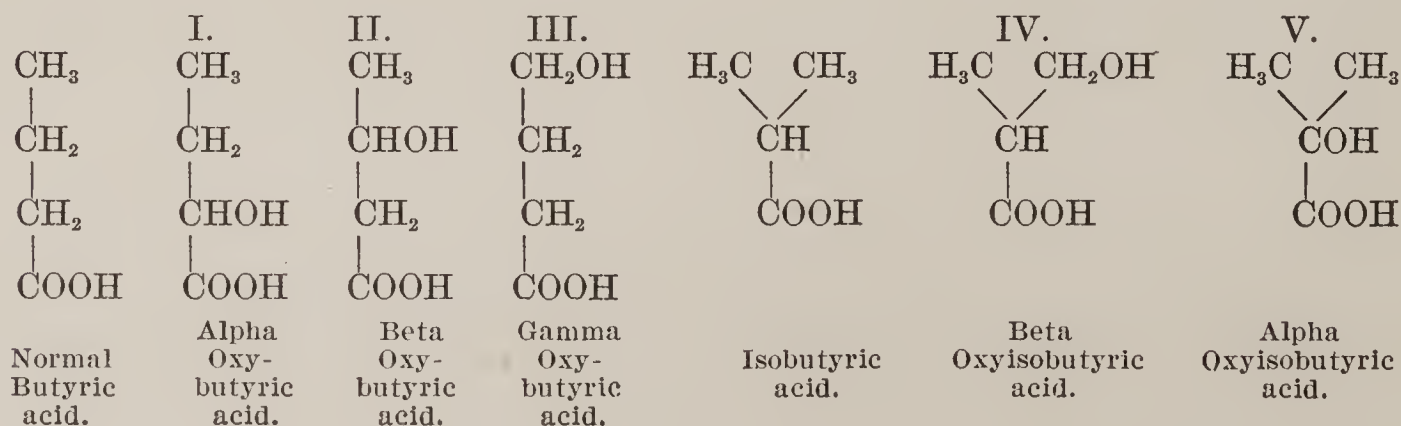
(4) From the aldehydes and ketones, by their conversion, first into oxycyanides by the action of hydrocyanic acid:



and the action upon these of acids or alkalies:

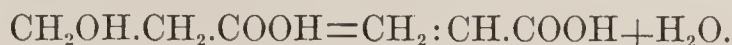


Isomeres—Position or Place Isomery.—Considering the oxybutyric acids as derived from normal and isobutyric acids by substitution of one OH for a hydrogen atom in a hydrocarbon group, the following five derivatives are possible:



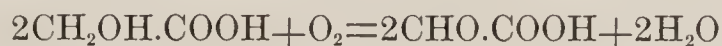
While III, IV, and V are obviously different in molecular structure from each other and from I and II, in that the latter contain the group CHOH, while the former contain the groups CH₂OH, CH, and COH, the only difference between I and II, whose molecules are composed of identical groups, is in the *position* or *place* of the alcoholic hydroxyl with reference to the carboxyl group. **Place isomer**es of this kind are distinguished by designating that in which the second substituted group (in this case the OH) is attached to the carbon atom contiguous to the first as the alpha, or 1-compound, and the others by the succeeding Greek letters, or by the numerals in the order of the removal of the position of the second substitution. Thus II above is Beta oxybutyric or 2-oxybutyric acid. (See Orientation, p. 337.)

The α , β , γ , and δ acids differ in their products of dehydration: The α acids yield cyclic double esters, called **lactids**, by elimination of H₂O from two molecules of the acid. The β acids are converted into unsaturated acids by loss of H₂O from one molecule of the acid:

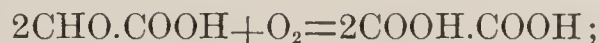


The γ and δ acids and those of greater carbon content, are converted into simple cyclic esters, called **lactones**, by elimination of H₂O from a single molecule of the acid.

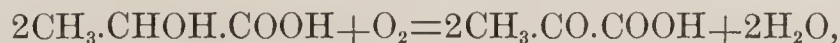
By further oxidation the primary oxyacids containing CH₂OH yield aldehyde acids:



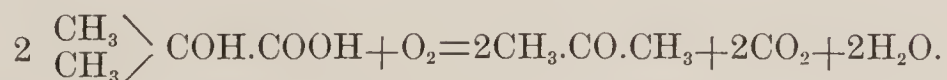
and then dibasic acids:



The secondary acids, containing CHOH, yield ketone acids:

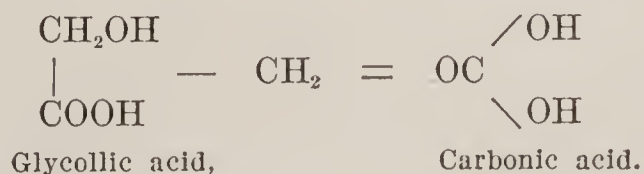


And the tertiary acids, containing COH, yield ketones, carbon dioxide and water:



The hydrogen of their carboxyl group may be replaced to form salts, esters, or amides; and the hydroxyl of their alcoholic group may be replaced by alkali metals, alkyls, or acylyls. In other words, they behave as acids and as alcohols.

Oxyformic Acid—Carbonic acid—OC(OH)₂.—Although this acid does not exist free, but is decomposed as soon as liberated into CO₂ and H₂O, its salts, the carbonates, are well known and quite stable. The position of this acid in this series is an apparent anomaly, as it is dibasic, not monobasic like the other terms of the series. But if we bear in mind that the basic nature of the H atom in a hydroxyl depends upon its close union with a CO group (or some other electro-negative group), it is evident that the two H atoms in the inferior homologue of glycollic acid, being similarly united to the same CO group, must be equally basic:



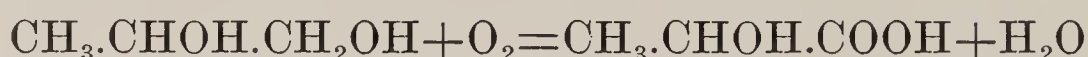
Indeed, carbonic acid is not an alcohol acid, but a pure acid, as it contains no alcoholic group.

Esters are also known corresponding to **orthocarbonic acid**: $\text{C}(\text{OH})_4$ although the acid itself is unknown.

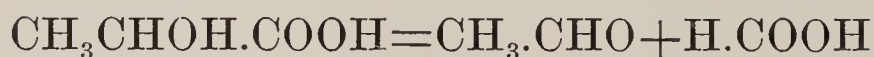
Glycollic Acid—Oxyacetic acid— $\text{CH}_2\text{OH}.\text{COOH}$ —is formed by the oxidation of glycol, by the action of nitrous acid upon glycol, and by the action of KOH upon monochloroacetic acid, or upon glyoxal, $\text{CHO}.\text{CHO}$.

It forms deliquescent acicular crystals, very soluble in water, alcohol and ether. It fuses at 80° . It is oxidized by HNO_3 to oxalic acid.

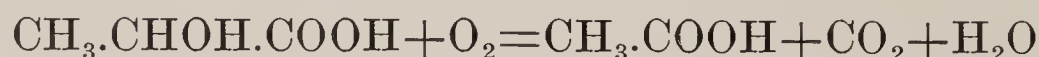
Lactic Acids—Oxypropionic acids—Alpha oxypropionic acid—Ethidene lactic acid— $\text{CH}_3.\text{CHOH}.\text{COOH}$ —is formed from milk sugar, cane sugar, gum and starch by *lactic fermentation*, induced by the lactic acid bacillus. It consequently exists in many soured products, such as soured milk, sour-kraut, fermented beet-juice, and the waste liquors of starch works and of tanneries. It is formed in the stomach during digestion of carbohydrates. It is prepared by allowing a mixture of cane sugar, tartaric acid, rotten cheese, skim milk and chalk to ferment for ten days at 35° . It has also been obtained by oxidation of alpha propylene glycol:



Lactic acid of fermentation is a colorless, or yellowish, syrupy liquid; sp. gr. 1.215 at 20° ; soluble in water, alcohol and ether. It does not distil without decomposition, but when heated it yields lactid, carbon monoxide, aldehyde and water. Heated to 130° with dilute sulphuric acid it splits into aldehyde and formic acid:



Oxidizing agents convert it into pyruvic acid: $\text{CH}_3.\text{CO}.\text{COOH}$, or, if more energetic, split it up into acetic acid and carbon dioxide:

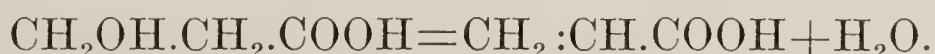


Hydriodic acid reduces it to propionic acid; but hydrobromic acid converts it into α -bromopropionic acid.

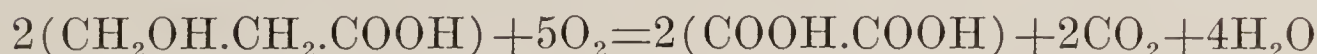
Ethidene lactic acid contains an asymmetric carbon atom (p. 239): $\text{CH}_3.\text{C}^*\text{HOH}.\text{COOH}$; and that produced by lactic fermentation is optically inactive ($d+1$). The **dextro** acid, also known as **sarcosyllactic** or **paralactic acid**, is best obtained from Liebig's meat extract; and is also produced by allowing *Penicillium glaucum* to grow in a solution of inactive ammonium lactate. It exists in muscular tissue after death and during contraction, and in the spleen, lymphatic glands, thymus, thyroid, blood, bile, transudates, in the perspiration in puerperal fever, and in the urine after violent exercise, in yellow atrophy of the liver and in phosphorus poisoning, either free or in combination. The acid in muscular tissue probably originates from glycogen.

Lævolactic Acid is formed by the growth of *Bacillus acidi lævolactici* in a solution of cane sugar.

Ethylene Lactic Acid—Beta oxypropionic acid—Hydracrylic acid— $\text{CH}_2\text{OH}.\text{CH}_2.\text{COOH}$ —the third form of lactic acid, is formed by the action of moist silver oxide upon β -iodo- or β -chloropropionic acid; by the saponification of ethylene cyanhydrine; or by the oxidation of the corresponding glycol. It is a thick, uncrystallizable syrup, which is converted by dehydration into acrylic acid:



On oxidation it yields oxalic acid and carbon dioxide:



Oxybutyric Acids.—Five isomeres are possible (p. 260). **Beta oxybutyric acid**— $\text{CH}_3.\text{C}^*\text{HOH}.\text{CH}_2.\text{COOH}$, is formed by the action of sodium amalgam upon acetoacetic ester: $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COOH} + \text{H}_2 = \text{CH}_3.\text{CHOH}.\text{CH}_2.\text{COOH}$. The lævo-acid, a colorless syrup, readily soluble in water, alcohol and ether, occurs, accompanied by acetoacetic acid, in the blood and urine in severe cases of diabetes.

MONOXYDICARBOXYLIC SERIES— $\text{C}_n\text{H}_{2n-2}\text{O}_5$.

The acids of this series contain two carboxyls and one alcoholic group. They are, therefore, dibasic and triatomic, and may be considered as derived from the glycerols by oxidation of both CH_2OH groups. They may also be considered as derived from the paraffin dicarboxylic acids (oxalic series), above the first, by substitution of OH for H in a hydrocarbon group, in the same manner as the acids of the oxyacetic series are derived from those of the acetic series.

Tartronic Acid—Oxymalonic acid— $\text{COOH}.\text{CHOH}.\text{COOH}$ —is formed by the action of moist silver oxide upon monochloro- or monobromo-malonic acid, or by oxidation of glycerol by potassium permanganate. It crystallizes in large prisms, readily soluble in water, alcohol, and ether, and fusible at 184° .

Malic Acid—Oxysuccinic acid— $\text{COOH}.\text{CH}_2.\text{C}^*\text{HOH}.\text{COOH}$ —exists in three modifications. The lævo-acid exists free, and in combination with K, Na, Ca, Mg, and organic bases in apples, pears, and similar fruits, and in the berries of the mountain ash and in gooseberries. The inactive (d+l) acid may be obtained from monobromo-succinic acid by the action either of moist silver oxide, of dilute HCl, of dilute NaOH, or even of boiling water; and by several other methods. The dextro-acid is obtained by the reduction of dextro-tartaric acid by hydriodic acid.

The natural malic acid crystallizes in prismatic needles; odorless; acid in taste; fusible at 100° ; deliquescent; very soluble in water and in alcohol. Heated to 140° it loses water with formation of fumaric acid, $\text{COOH}.\text{CH}:\text{CH}.\text{COOH}$.

At 180° it yields water, fumaric acid and maleic anhydride, $\begin{array}{c} \text{CH.CO} \backslash \\ || \quad \quad \text{O} \\ \text{CH.CO} / \end{array}$.

Reducing agents convert it into succinic acid. The malates are oxidized to carbonates in the body.

Oxyglutaric Acid exists in the two isomeres: α oxyglutaric acid, $\text{COOH}.\text{CH}(\text{OH}).\text{CH}_2.\text{CH}_2.\text{COOH}$, which occurs in molasses, crystallizes with difficulty, and fuses at 72° ; and β oxyglutaric acid, $\text{COOH}.\text{CH}_2.\text{CHOH}.\text{CH}_2.\text{COOH}$, which fuses at 95° .

DIOXYDICARBOXYLIC ACIDS— $C_nH_{2n-2}O_6$.

Tartaric Acids—Dioxyethylene Succinic Acids.— $COOH.CHOH.CHOH.COOH$ (and see p. 160)—There exist four acids having the composition $C_4H_6O_6$, which are readily convertible one into the other. They are: *Dextro-tartaric*, or *ordinary tartaric acid*; *laevo-tartaric acid*; *mesotartaric*, or *antitartaric acid*; and *racemic*, or *paratartaric acid*. The first three of these are stereoisomeres, due to the presence of two asymmetric carbon atoms in the molecule, whose molecular structure has been discussed under the head of space isomery (p. 239). Mesotartaric acid, which is optically inactive, has a molecular structure differing from those of the d- and l- acids, into which it cannot be split. Racemic acid, also optically inactive, is the (d+l) acid, and can be readily decomposed into them or separated from a mixture of them.

Dextro-tartaric Acid—Ordinary tartaric acid—Acidum tartaricum (U. S. P.)—occurs, both free and in combination, in the sap of the vine and in many other vegetable juices and fruits, particularly in grape-juice. Although this is probably the only tartaric acid existing in nature, all four varieties may occur in the commercial acid, being formed during the process of manufacture. Tartaric acid is obtained in the arts from hydropotassic tartrate, or cream of tartar.

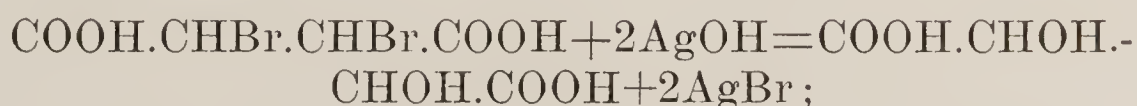
The ordinary tartaric acid crystallizes in large prisms; very soluble in H_2O and in alcohol; acid in taste and reaction. Heated with water at 165° – 175° it is converted into mesotartaric and racemic acids: It fuses at 170° ; at 180° it loses H_2O , and is gradually converted into an anhydride; at 200° – 210° it is decomposed with formation of **pyruvic acid**, $C_3H_4O_3$, and **pyrotartaric acid**, $C_5H_8O_4$; at higher temperatures CO_2 , CO , H_2O , hydrocarbons and charcoal are produced.

Tartaric acid is attacked by oxidizing agents with formation of CO_2 , H_2O , and, in some instances, formic and oxalic acids. Certain reducing agents convert it into malic and succinic acids. With fuming HNO_3 it forms a dinitro-compound, which is very unstable, and which, when decomposed below 36° , yields tartaric acid. It forms a precipitate with lime-water, soluble in an excess of H_2O . In not too dilute solution it forms a precipitate with potassium sulphate solution. It does not precipitate with the salts of Ca. When heated with a solution of auric chloride it precipitates the gold in the metallic form.

When taken into the economy, as it frequently is in the form of tartrates, the greater part is oxidized to carbonic acid (carbonates); but, if taken in sufficient quantity, a portion is excreted unchanged in the urine and perspiration. The free acid is poisonous in large doses. The acids and its salts are largely used in pharmacy and in dyeing. (See p. 160.)

Lævo-tartaric—forms crystals similar to those of the dextro acid, but having opposite hemihedral facets, so that the crystals of one acid resemble the reflection of those of the other in a mirror.

Racemic Acid—(*d+l*) *Tartaric acid*—is produced when concentrated solutions of equal quantities of d- and l-tartaric acids are mixed. It is formed by oxidation of dulcitol and of mannitol. It is obtained by the action of moist silver oxide upon dibromo succinic acid:



and by several other synthetic methods. It crystallizes in rhombic prisms, less soluble in water than ordinary tartaric acid, and fuses at 205° .

Mesotartaric Acid—*Inactive Tartaric acid*—is obtained by oxidation of erythrol; or by heating dextrotartaric acid with water at 165° for two days.

HIGHER DICARBOXYLIC OXYACIDS.

The carbohydrates, on oxidation with nitric acid, yield *tetroxydicarboxylic acids*: $\text{COOH}(\text{CHOH})_4\text{COOH}$. Among these are: **mannosaccharic acids**; **saccharic acids**; and **mucic acid**. Of the three **saccharic acids** the d-acid is the best known. It is produced by oxidation of many carbohydrates, including cane sugar and grape sugar, by nitric acid, and by the action of bromine water on glucuronic acid. Nascent H reduces it to glucuronic acid. It forms a syrup or a deliquescent solid, which, on standing, changes to a crystalline lactone. **Mucic acid** is produced by the oxidation of dulcitol, milk sugar, and the gums. It is a white solid, almost insoluble in cold water and in alcohol, which fuses at 210° .

OXYTRICARBOXYLIC ACIDS— $\text{C}_n\text{H}_{2n-4}\text{O}_7$.

Citric Acid— $\text{HO.C} \begin{array}{l} \nearrow \text{CH}_2\text{COOH} \\ \text{—COOH} \\ \searrow \text{CH}_2\text{COOH} \end{array}$, exists in the juices of many fruits, lemon,

strawberry, currant, and in small quantity, as calcium citrate, in cow's milk. It is obtained commercially from lemon juice. It crystallizes in large, rhombic prisms, very soluble in water and in alcohol. It fuses at 100° ; at 175° it is decomposed with loss of water and formation of **aconitic acid**; and at a higher temperature CO_2 is given off and **citraconic** and **itaconic acids** are produced. In the body its salts are oxidized to carbonates.

ALDEHYDE-ACIDS.

These are substances having both aldehyde and acid functions, and containing the groups CHO and COOH. The simplest of the class is formic acid, already referred to as the first term of the acetic series, in which, however, the carbon atom is common to the two groups: $\text{O}:\text{C} \begin{array}{l} \nearrow \text{H} \\ \searrow \text{OH} \end{array}$.

Glyoxylic Acid— CHO.COOH —when produced unites with water to form a hydrate: $(\text{OH})_2:\text{CH.COOH}$, corresponding to chloral hydrate: $(\text{OH})_2:\text{CH.CCl}_3$.

This is a thick syrup, or it forms rhombic prisms. It is produced by heating dichloroacetic acid with water at 230° :



It has the reducing power and other properties of the aldehydes.

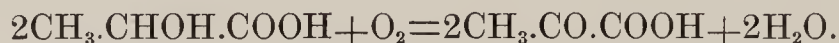
KETONE-ACIDS.

These compounds contain both the ketonic and carboxyl groups, CO and COOH.

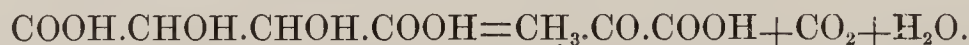
The **monoketone-monocarboxylic acids** contain one CO and one COOH. According as the CO group occupies the position adjacent to the carboxyl, or further removed therefrom, these acids are designated as α , β , γ , etc.; thus $\text{CH}_3.\text{CH}_2.\text{CO}.\text{COOH} = \alpha$, $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COOH} = \beta$, etc.

The α , γ , δ , etc., acids are much more stable than the β -acids, and may be obtained by oxidation of the corresponding secondary alcohol acids. The α acids are derivable from formic acid by substitution of acidyls for the extra-carboxylic hydrogen: $(\text{CH}_3.\text{CO}).\text{COOH}$.

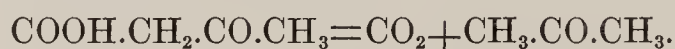
Pyruvic Acid—*Pyroracemic acid*— $\text{CH}_3.\text{CO}.\text{COOH}$ —is formed by oxidation of α -oxypropionic acid:



It is also formed by distillation of tartaric acid:



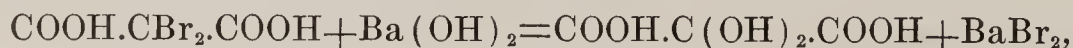
The β -ketone acids are more unstable, and are decomposed by heat with formation of ketone and carbon dioxide:



Their esters are, however, quite stable, and are employed in many syntheses. The β acids bear the same relation to acetic acid that the α acids do to formic acid: $(\text{CH}_3.\text{CO}).\text{CH}_2.\text{COOH}$.

Aceto-acetic Acid—**Diacetic Acid**— $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COOH}$ —may be obtained as a thick, strongly acid liquid by saponification of its esters. Heat decomposes it into acetone and carbon dioxide, according to the equation given above. Aceto-acetic acid accompanies β oxybutyric acid and acetone in the urine in diabetes. (See Aceto-acetic ester, p. 278).

Mesoxalic Acid—**Dioxymalonic acid**— $\begin{array}{c} \text{HO} \backslash \\ \text{HO} / \end{array} \text{C} \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$ —is the monoketone-dicarboxylic acid, $\text{COOH}.\text{CO}.\text{COOH}$, combined with water in the same manner as chloral hydrate and glyoxylic acid. Esters are known corresponding to both forms: **oxymalonic esters**, $\text{CO}:(\text{COO}.\text{C}_2\text{H}_5)_2$, and **dioxymalonic esters**, $\text{C}(\text{OH})_2:(\text{COO}.\text{C}_2\text{H}_5)_2$. Mesoxalic acid is obtained by the action of boiling barium hydroxide upon dibromomalonic acid:



or upon alloxan (mesoxalylurea). It crystallizes in prisms, very soluble in water, fusible at 115° . On evaporation of its aqueous solution it decomposes into carbon monoxide, water and oxalic acid; at higher temperatures it yields carbon dioxide and glyoxylic acid.

OXYALDEHYDE AND OXYKETONE ACIDS.

These acids contain alcoholic groups, CH_2OH , CHOH , or COH in addition to carboxyl and either the aldehyde or ketone group, CHO or CO.

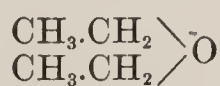
Glucuronic Acid— $\text{CHO}.\text{(CHOH)}_4.\text{COOH}$ —is a derivative of glucose: $\text{CHO}.\text{(CHOH)}_4.\text{CH}_2\text{OH}$. It is a syrup which passes into a crystalline lactone

on warming. It occurs in the urine in small quantity normally, in combination with phenol, skatole and indole, and with camphors, chloral and other substances when these are present.

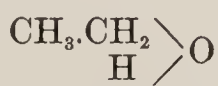
SIMPLE ETHERS.

These substances have been referred to (p. 209) as the simplest products of oxidation of the hydrocarbons. The term *ether* was formerly applied to any substance produced by the action of an acid upon an alcohol. Such products belong, however, to two distinct classes:

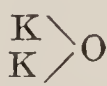
(1) **The simple ethers, or ethers**, which are the oxides of the hydrocarbon radicals, and the counterparts of the metallic oxides, bearing the same relation to the alcohols that the metallic oxides do to their hydroxides:



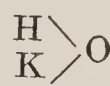
Ethyl oxide.
(Ether.)



Ethyl hydroxide.
(Alcohol).

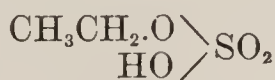


Potassium
oxide.

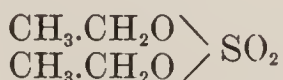


Potassium
hydroxide.

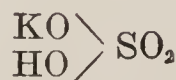
(2) **The compound ethers**, now called **esters**, which are the products of the reaction between an acid and the alcohol, the latter behaving as a basic hydroxide. They are the counterparts of the metallic salts:



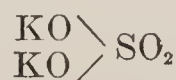
Monoethylic
sulphate.
(Ester-acid.)



Diethylic
sulphate.
(Neutral ester.)



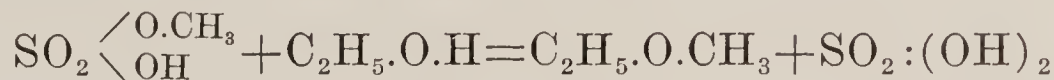
Monopotassic
sulphate.
(Acid salt.)



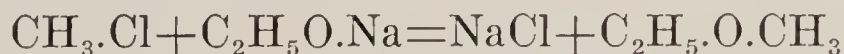
Dipotassic
sulphate.
(Neutral salt.)

Mixed ethers differ from simple ethers in that they contain different, in place of similar, alkyls, as **methyl-ethyl oxide**: $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$.

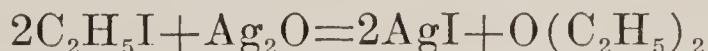
Simple and mixed ethers are formed: (1) By interaction of the alcohols and alkyl-sulphuric acids. Thus methyl-sulphuric acid and ethylic alcohol form methyl-ethyl oxide:



(2) By the action of alkyl halides upon sodium alcoholates:



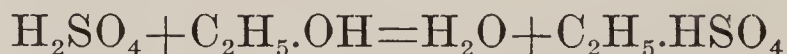
(3) By the action of silver oxide upon alkyl halides:



Methyl oxide— $\text{CH}_3\cdot\text{O}\cdot\text{CH}_3$ —46—isomeric with ethyl alcohol, is obtained by the action of silver oxide upon methyl iodide, or by the action of H_2SO_4 and boric acid upon methyl alcohol. It is a colorless gas, has an ethereal odor, burns with a pale flame, liquefies at -36° and boils at -21° , is soluble in H_2O , H_2SO_4 and ethylic alcohol.

Ethyl Oxide—*Ethylic ether*—*Sulphuric ether*—*Æther* (U. S. P.)— $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$.—In the manufacture of ether a mixture is made of 5 pts. of 90% alcohol and 9 pts. of concentrated H_2SO_4 , in a vessel surrounded by cold water. This mixture is introduced into a retort, into which a slow stream of alcohol is allowed to flow during the remainder of the process. Heat, so regulated as not to exceed 140° , is then applied to the retort, which is connected with a well-cooled condenser, and continued until the temperature rises above the point indicated. The distillate contains ether, alcohol, water and dissolved gases, notably SO_2 . It is shaken with water containing potash or lime, and the ether decanted off. The product is “washed ether.” For further purification it is treated with calcium chloride, or recently burnt lime, with which it is left in contact for 24 hours, and from which it is then distilled.

In the conversion of alcohol into ether, sulphovinic or ethyl-sulphuric acid behaves as a “contact substance” and serves to carry an ethyl radical from one alcohol molecule to another, with formation of water and regeneration of sulphuric acid. In the first stage of the reaction ethyl-sulphuric acid is formed by the action of H_2SO_4 upon alcohol, molecule for molecule:



The ethyl-sulphuric acid then reacts with another molecule of alcohol, according to the general reaction (1) for the formation of ethers, to form ether and sulphuric acid:



It would seem, therefore, that a given quantity of H_2SO_4 could convert an unlimited amount of alcohol into ether. But the gradual accumulation of the H_2O formed in the first stage of the reaction, and the occurrence of secondary reactions in practice limit the amount of ether produced to about four or five times the bulk of acid used.

Ether is a colorless liquid; has a sharp, burning taste, and a peculiar, tenacious odor, characterized as ethereal. Sp. gr. 0.723 at 12.5° ; it boils at 34.5° . Its tension of vapor is very great, especially at high temperatures; and it is exceedingly volatile. Water dissolves one-ninth its weight of ether. Ethylic and methylic alcohols are miscible with it in all proportions. Ether is an excellent solvent of many substances not soluble in water and alcohol. The resins and fats are readily soluble in ether. The salts of the alkaloids and many vegetable coloring matters are soluble in alcohol and water, but insoluble in ether, while the free alkaloids are for the most part soluble in ether, but insoluble, or very sparingly soluble, in water.

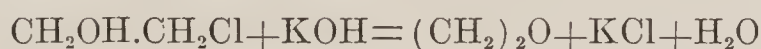
Ether is highly inflammable; and burns with a luminous flame. The vapor forms with air a violently explosive mixture. It is denser than air, through which it falls and diffuses itself to a great dis-

tance; caution is therefore required in handling ether in a locality in which there is a light or fire, especially if the fire be near the floor.

Pure ether is neutral in reaction. H_2SO_4 mixes with it, with elevation of temperature, and formation of sulphovinic acid. With sulphuric anhydride it forms ethyl sulphate. HNO_2 , aided by heat, oxidizes it to carbon dioxide and acetic and oxalic acids. Ether, saturated with HCl and distilled, yields ethyl chloride. Cl , in the presence of H_2O , oxidizes it, with formation of aldehyde, acetic acid, and chloral. In the absence of H_2O , however, a series of products of substitution are produced, in which 2, 4, and 10 atoms of H are replaced by a corresponding number of atoms of Cl . These substances in turn, by substitution of alcoholic radicals, or of atoms of elements, for atoms of Cl , give rise to other derivatives.

Ethylene Oxide— $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{O}$ —is a cyclic ether corresponding to glycol: $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}=(\text{CH}_2)_2\text{O}+\text{H}_2\text{O}$, as ethyl oxide corresponds to ethylic alcohol: $2\text{CH}_3.\text{CH}_2.\text{OH}=(\text{C}_2\text{H}_5)_2\text{O}+\text{H}_2\text{O}$

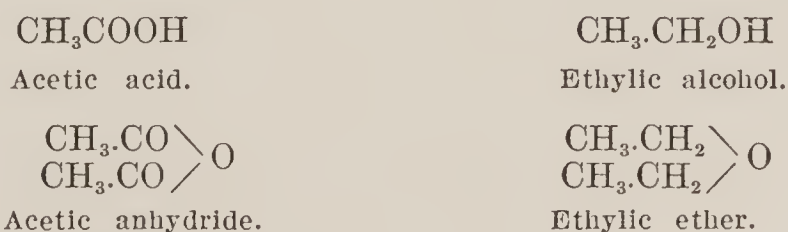
It is prepared by the action of caustic potash on ethylene chlorhydrine:



It is a volatile liquid, boils at 13.5° , is neutral in reaction and mixes with water. It unites with H_2O to form glycol, and with HCl to regenerate ethylene chlorhydrine. Nascent H converts it into ethyl alcohol.

ACID ANHYDRIDES.

The acid anhydrides are the oxides of the acid radicals (acidyls); and bear the same relation to the acids that the simple ethers bear to the alcohols:



The acid anhydrides of the monobasic acids are produced by the action of the acidyl chlorides upon anhydrous salts:



or by the action of phosphorus oxychloride upon the alkali salts of the acids. In this method of formation the acidyl chloride is first produced:



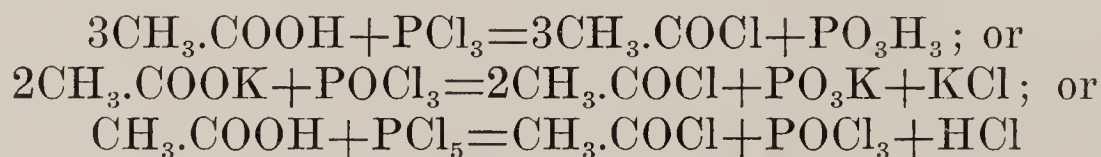
and this acts upon an excess of the salt according to the above equation. Formic acid produces no anhydride.

Acetic Anhydride— $(\text{C}_2\text{H}_3\text{O})_2\text{O}$ —is a pungent liquid which boils

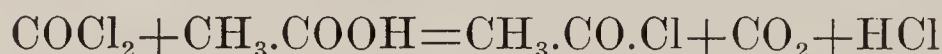
at 137° . It is formed by the general methods and also by heating lead acetate with carbon disulphide at 165° . It serves for the introduction of the radical acetyl into other molecules.

ACIDYL HALIDES.

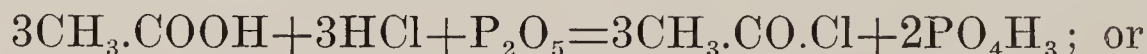
These compounds, also known as halide anhydrides, are the halogen compounds of the acidyls. They are produced: (1) By the action of the phosphorus halides upon the acids or their salts:



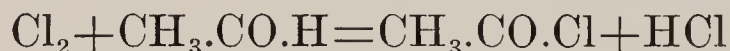
(2) By the action of phosgene upon the acids, or their salts:



(3) By the action of phosphorus pentoxide upon the acids in presence of hydrochloric acid:



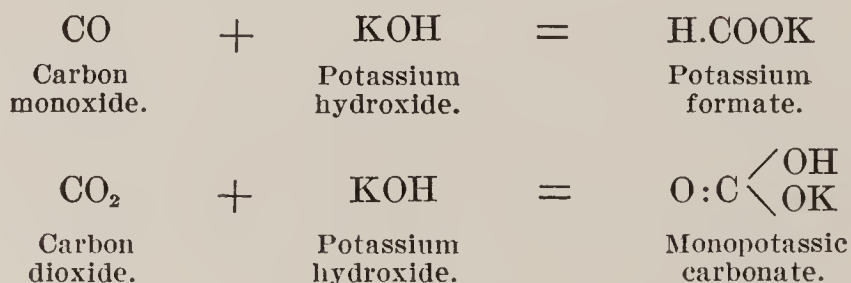
(4) By the action of chlorine upon the aldehydes:



Acetyl Chloride— $\text{CH}_3.\text{CO.Cl}$ —is a colorless, pungent liquid, which boils at 55° . It is decomposed by water with formation of acetic and hydrochloric acids. With acetic acid it forms acetic anhydride. It is used to produce acetyl derivatives.

OXIDES OF CARBON.

The two oxides of carbon are also anhydrides in that they combine with water to produce acids, or, what amounts to the same thing, with KOH to form the K salts, thus:



Carbon Monoxide—Carbonous oxide—Carbonic oxide—CO—28—is formed: (1) By burning C with a limited supply of air.

(2) By passing dry carbon dioxide over red-hot charcoal.

(3) By heating oxalic acid with sulphuric acid:



and passing the gas through sodium hydroxide to separate CO₂.

(4) By heating potassium ferrocyanide with H₂SO₄.

It is a colorless, tasteless gas: sp. gr. 0.9678A; very sparingly soluble in H_2O and in alcohol. It burns in air with a blue flame to CO_2 , and it forms explosive mixtures with air and oxygen. It is a valuable reducing agent, and is used for the reduction of metallic oxides at a red heat. Ammoniacal solutions of the cuprous salts absorb it readily. Being non-saturated, it unites readily with O to form CO_2 , and with Cl to form $COCl_2$, the latter a colorless, suffocating gas, known as **phosgene**, or **carbonyl chloride**, which is of service in the formation of acid chlorides and anhydrides and in a variety of other syntheses.

Toxicology.—Carbon monoxide is an exceedingly poisonous gas, and is the chief toxic constituent of the gases given off from blast-furnaces, from defective flues, from open coal or charcoal fires and of illuminating gas.

Poisoning by CO may occur in several ways. By inhalation of the gases discharged from blast-furnaces and from copper-furnaces, the former containing 25 to 32 per cent. and the latter 13 to 19 per cent. of CO. By the fumes given off from charcoal burned in a confined space, which consists of a mixture of the two oxides of carbon, the dioxide predominating largely, especially when the combustion is most active. The following is the composition of an atmosphere produced by burning charcoal in a confined space, and which proved rapidly fatal to a dog: oxygen, 19.19; nitrogen, 76.62; carbon dioxide, 4.61; carbon monoxide, 0.54; marsh-gas, 0.04. Obviously the deleterious effects of charcoal-fumes are more rapidly fatal in proportion as the combustion is imperfect and the room small and ill-ventilated.

A fruitful source of CO poisoning, sometimes fatal, but more frequently producing languor, headache and debility, is to be found in the stoves, furnaces, etc., used in heating our dwellings and other buildings, especially when the fuel is anthracite coal. This fuel produces in its combustion, when the air supply is not abundant, considerable quantities of CO, to which a further addition may be made by the reduction of the dioxide, also formed, passing over red-hot iron.

Fatal poisoning by illuminating gas is of very frequent occurrence. The most actively poisonous ingredient of illuminating gas is CO, which exists in ordinary coal-gas in the proportion of 4 to 7.5 per cent., and in water-gas, made by decomposing superheated steam by passage over red-hot coke, and subsequent charging with vapor of hydrocarbons, in the large proportion of 30–35 per cent.

The *method* in which CO produces its fatal effects is by forming with the blood-coloring matter a compound which is more stable than oxyhemoglobin, and thus causing asphyxia by destroying the power of the blood corpuscles of carrying O from the air to the tissues. This compound of CO and hemoglobin is quite stable, and hence the symptoms of this form of poisoning are very persistent, lasting until the place of the coloring-matter thus rendered useless is supplied by new formation. The *prognosis* is very unfavorable when the amount of the gas inhaled has been at all considerable, the *treatment* usually followed, *i.e.*, artificial respiration and inhalation of O, restoring the altered coloring matter very slowly. There would seem to be no form of poisoning in which transfusion of blood is more directly indicated than in that by CO, but it has been found to be detrimental rather than beneficial.

Detection after death.—The blood of those asphyxiated by CO is persistently bright-red in color. When suitably diluted and examined with the spectroscope, it presents an absorption spectrum (No. 6, Fig. 19, p. 273) of two bands similar to that of oxyhemoglobin (No. 3, Fig. 19), but in which

the two bands are more equal and somewhat nearer the violet end of the spectrum. Owing to the greater stability of the CO compound, its spectrum may be readily distinguished from that of the O compound by the addition of a reducing agent (an ammoniacal solution of ferrous tartrate), which changes the spectrum of oxyhemoglobin to the single-band spectrum of hemoglobin (No. 1, Fig. 19), while that of the CO compound remains unaltered, or only fades partially.

If a solution of caustic soda of sp. gr. 1.3 is added to normal blood, a black, slimy mass is formed, which, when spread upon a white plate, has a greenish-brown color. The same reagent added to blood altered by CO forms a firmly clotted mass, which in thin layers upon a white surface is bright red in color.

A piece of gun-cotton upon which platinum-black has been dusted fires in air containing 2.5 in 1,000 of CO.

Carbon Dioxide—Carbonic anhydride—Carbonic acid gas— CO_2 —44—is obtained: (1) By burning C in air or O. (2) By decomposing a carbonate (marble= CaCO_3) by a mineral acid (HCl diluted with an equal volume of H_2O).

At ordinary temperatures and pressures it is a colorless, suffocating gas; has an acidulous taste; sp. gr. 1.529 A; soluble in an equal volume of H_2O at the ordinary pressure, much more soluble as the pressure increases. **Soda water** is a solution of carbonic acid in H_2O under increased pressure. When compressed to the extent of 38 atmospheres at 0° ; 50 atm. at 15° ; or 73 atm. at 30° it forms a transparent, mobile liquid, by whose evaporation, when the pressure is relieved, sufficient cold is produced to solidify a portion into a snow-like or ice-like mass, which, by spontaneous evaporation in air, produces a temperature of -90° .

Carbon dioxide neither burns nor does it support combustion. When heated to $1,300^\circ$, it is dissociated into CO and O. A similar decomposition is brought about by the passage through it of electric sparks. When heated with H it yields CO and H_2O . When K, Na, or Mg is heated in an atmosphere of CO_2 , the gas is decomposed with formation of a carbonate and separation of carbon. When caused to pass through solutions of the hydroxides of Na, K, Ca, or Ba, it is absorbed, with formation of the carbonates of those metals, which, in the case of the last two, are deposited as white precipitates. Solution of potash is frequently used in analysis to absorb CO_2 , and lime and baryta water as tests for its presence. The hydroxides mentioned also absorb CO_2 from moist air.

Atmospheric Carbon Dioxide.—Carbon dioxide exists in free country air in the proportion of about four parts in 10,000. Its sources are from: (1) Respiration. Expired air contains about 4.5 per cent. CO_2 . (2) Combustion of fuel, illuminating gas, etc. A burner consuming three cubic feet of illuminating gas per hour produces as much CO_2 as is formed by the respiration of seven human beings. In a confined space respiration and combustion vitiate the

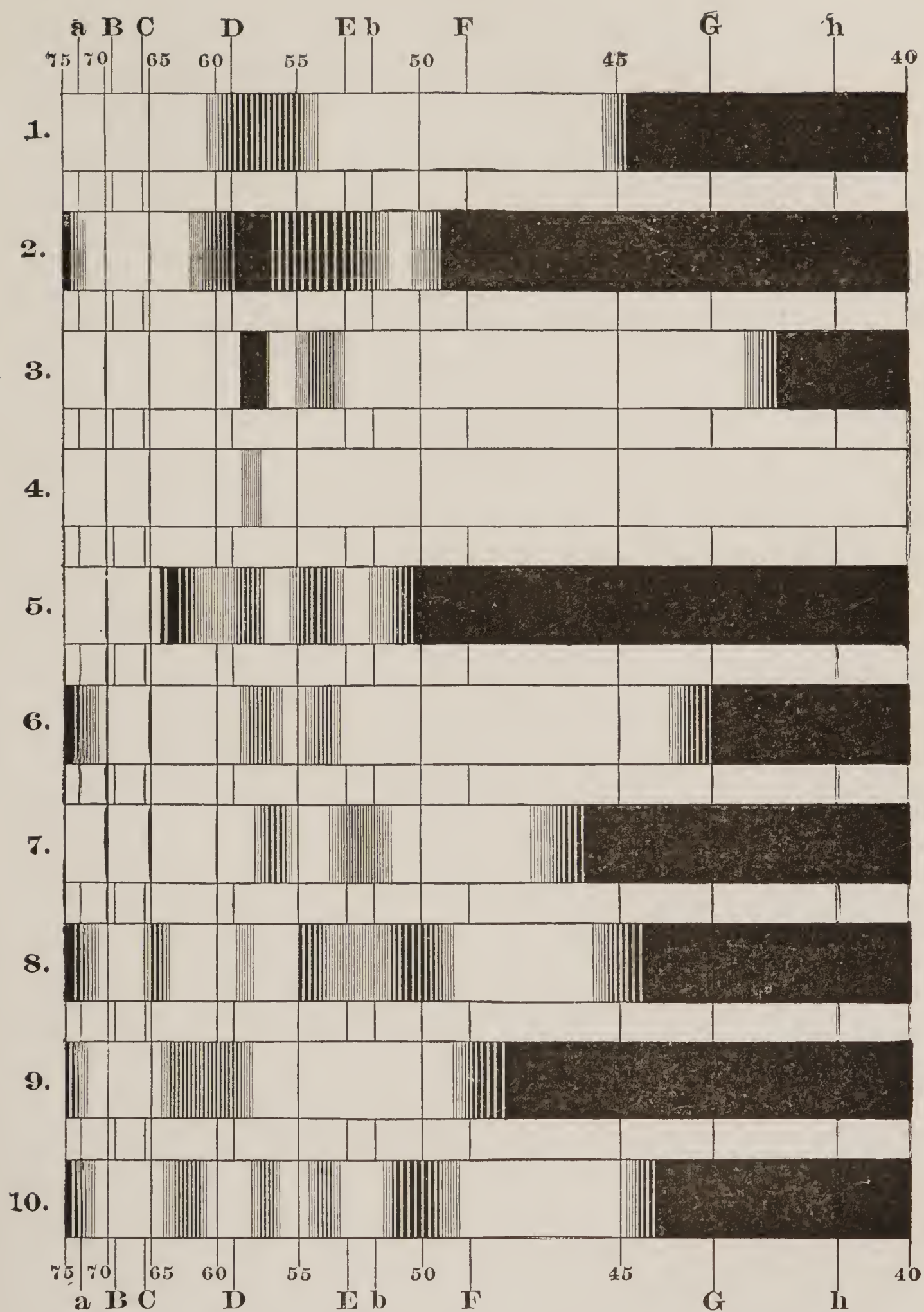


FIG. 19. Spectra of: (1) Reduced hemoglobin; (2) Oxyhemoglobin, concentrated; (3) Same, dilute; (4) Same, very dilute; (5) Methemoglobin, in faintly alkaline solution; (6) Carbon monoxide hemoglobin; (7) Hemochromogen, in alkaline solution; (8) Hematin, in acid solution; (9) Hematin, in alkaline solution; (10) Hematoporphyrin, in acid solution.

air in two ways: by addition of carbon dioxide and by removal of oxygen, as the CO_2 is produced at the expense of atmospheric oxygen. By the other methods of its origin it is merely added to the air, whose oxygen-content remains nearly unaltered. (3) Fermentation. For every liter of alcohol produced 384 liters of CO_2 are added to the air. (4) Tellural sources, such as volcanic fissures, volcanoes, spring waters. (5) Manufacturing operations, such as lime-burning, cement and brick-making, iron furnaces, etc. (6) In coal mines the *after-damp* contains a volume of CO_2 equal to that of the fire-damp exploded.

Notwithstanding the large amounts of CO_2 discharged into the atmosphere from these several sources, and it is estimated that the amount is sufficient to double the atmospheric CO_2 -content in about eighty years, no increase in the normal proportion of CO_2 in free air has been observed. This is due to the constant removal of CO_2 from the air by plants, the green pigment of which, **chlorophyll**, decomposes CO_2 under the influence of sunlight, retaining the carbon in organic combination, and returning oxygen to the air.

Action on the Economy.—An animal introduced into an atmosphere of pure CO_2 dies almost instantly, and without entrance of the gas into the lungs, death resulting from spasm of the glottis, and consequent apnœa.

When the proportion of O is not diminished, the poisonous action of CO_2 is not as manifest, in equal quantities, as when the air is poorer in oxygen. An animal will die rapidly in an atmosphere composed of 21 per cent. O, 59 per cent. N, and 20 per cent. CO_2 by volume; but will live for several hours in an atmosphere whose composition is 40 per cent. O, 37 per cent. N, 23 per cent. CO_2 . If CO_2 is added to normal air, of course the relative quantity of O is slightly diminished, while its absolute quantity remains the same. This is the condition of affairs existing in nature when the gas is discharged into the air. Under these circumstances an addition of 10–15 per cent. of CO_2 renders an air rapidly poisonous, and one of 5–8 per cent. will cause the death of small animals more slowly. Even a less proportion than this may become fatal to an individual not habituated.

When present in large proportion, CO_2 produces immediate loss of muscular power, and death without a struggle; when more dilute, a sense of irritation of the larynx, drowsiness, pain in the head, giddiness, gradual loss of muscular power, and death in coma.

If the CO_2 present in air is produced by respiration, or combustion, the proportion of O is at the same time diminished, and much smaller absolute and relative amounts of the poisonous gas will produce the effects mentioned above. Thus, an atmosphere containing in volumes 19.75 per cent. O, 74.25 per cent. N, 6 per cent. CO_2 , is much more rapidly fatal than one composed of 21 per cent. O, 59 per cent. N, 20 per cent. CO_2 . With a corresponding reduction of O, 5 per cent. of CO_2 renders an air sufficiently poisonous to destroy life; 2 per cent. produces severe suffering; 1 per cent. causes great discomfort, while 0.1 per cent., or even less, is recognized by a sense of closeness.

The treatment in all cases of poisoning by CO_2 consists in the inhalation of pure air (to which an excess of O may be added), aided, if necessary, by artificial respiration, the cold douche, galvanism, and friction.

Detection of Carbon Dioxide and Analysis of Confined Air.—Carbon dioxide, or air containing it, causes a white precipitate when caused to bubble

through lime or baryta water. Normal air contains enough of the gas to form a scum upon the surface of these solutions when exposed to it.

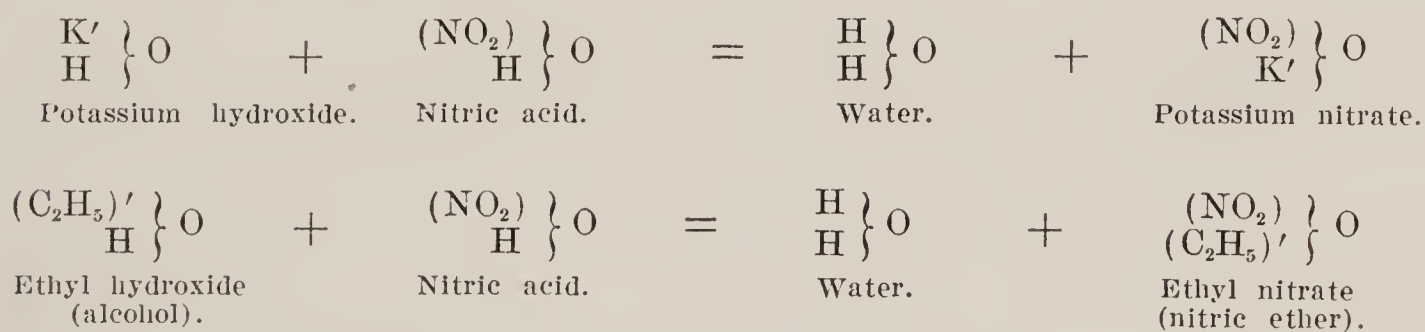
It was at one time supposed that air in which a candle continued to burn was also capable of maintaining respiration. This is, however, by no means necessarily true. A candle introduced into an atmosphere in which the normal proportion of O is contained, burns readily in the presence of 8 per cent. of CO₂; is perceptibly dulled by 10 per cent.; is usually extinguished with 13 per cent.; always extinguished with 16 per cent. Its extinction is caused by a less proportion of CO₂, 4 per cent., if the quantity of O be at the same time diminished. Moreover, a contaminated atmosphere may not contain enough CO₂ to extinguish, or perceptibly dim the flame of a candle, and at the same time contain enough of the monoxide to render it fatally poisonous if inhaled.

The presence of CO₂ in a gaseous mixture is determined by its absorption by a solution of potash; its quantity either by measuring the diminution in bulk of the gas, or by noting the increase in weight of an alkaline solution.

As the proportion of CO₂ in air is determinable readily and accurately, its determination in a confined air is depended upon to judge of the respirability of the air and the degree of perfection of the methods of ventilation used. For these purposes an air is condemned as vitiated if it contain more than six parts in 10,000 of CO₂.

ESTERS—COMPOUND ETHERS.

As the alcohols resemble the mineral bases, and the organic acids resemble those of mineral origin, so the esters are similar in constitution to the salts, being *formed by the double decomposition of an alcohol with an acid, mineral or organic*, as a salt is formed by double decomposition of an acid and a mineral base, the radical playing the part of an atom of corresponding valence:



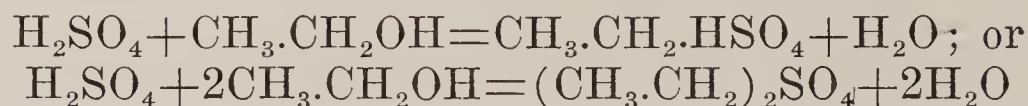
Therefore the esters are substances derived from acids by partial or complete substitution of an alkyl or alkyls for the basic hydrogen of the acid.

Some of the esters still contain a portion of the acid hydrogen which, being replaceable by another radical or by a metal, communicates acid qualities to the substance, which is at the same time an ester and a true acid. Such esters are the counter-parts of the acid salts. Or di- and polyhydric alcohols, in combining with acids of inferior basicity, may form esters which still retain alcoholic hydroxyls, and which are, therefore, **alcohol-esters**.

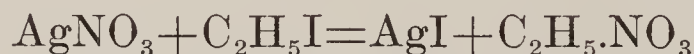
ESTERS OF THE MONOHYDRIC ALCOHOLS.

These esters are produced:

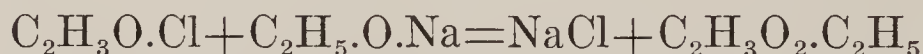
(1) By the action of the acid upon the alcohol:



(2) By the action of the corresponding haloid esters upon the silver salt of the acid:



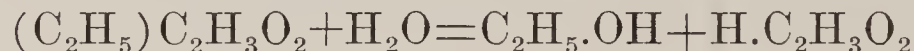
(3) By the action of the acidyl chlorides upon the sodium derivatives of the alcohols, and in some instances upon the alcohols themselves:



All esters are decomposed into acid and alcohols by the action of water at high temperatures, or of caustic potash or soda:



As this decomposition is analogous to that utilized in the manufacture of soap (p. 282), it is known as **saponification**, and whenever an ester is so decomposed it is said to be **saponified**. When the decomposition is effected by H_2O the free acid and the alcohol are formed, and it is known as **hydrolysis** (p. 64):



This reaction is reversible and therefore does not proceed to completion. Starting with the ester it is saponified according to the equation until equilibrium is established, but starting with alcohol and acid the reaction proceeds according to the equation read from right to left until the same condition is reached.

Ethyl Nitrate—*Nitric ether*— $\left. \begin{smallmatrix} \text{NO}_2 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$ —91.—A colorless liquid; has a sweet taste and bitter after-taste; sp. gr. 1.112 at 17° ; boils at 85° ; gives off explosive vapors. Prepared by distilling a mixture of HNO_3 and $\text{C}_2\text{H}_6\text{O}$ in the presence of urea.

Ethyl Nitrite—*Nitrous ether*— $\left. \begin{smallmatrix} \text{NO} \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right\} \text{O}$ —75—is prepared by directing nitrous fumes into alcohol, contained in a retort connected with a well-cooled receiver.

It is a yellowish liquid; has an apple-like odor, and a sharp, sweetish taste: sp. gr. 0.947; boils at 18° ; gives off inflammable vapor; very sparingly soluble in H_2O ; readily soluble in alcohol and ether. It is decomposed by warm H_2O and by alkalies.

Ethyl Sulphates— $(\text{C}_2\text{H}_5)\text{HSO}_4$ —*Ethyl sulphuric* or *sulphovinic acid* and $(\text{C}_2\text{H}_5)_2\text{SO}_4$ —*Ethyl sulphate*—*Sulphuric ether*.

Monoethylic sulphate—*Ethyl-sulphuric acid*— $\text{C}_2\text{H}_5\text{O} \begin{smallmatrix} \diagup \\ \text{HO} \end{smallmatrix} \text{SO}_2$ —is formed as an intermediate product in the manufacture of ethylic ether. It is a colorless, syrupy, highly acid liquid; sp. gr. 1.316; soluble in water and alcohol in all proportions, insoluble in ether.

It decomposes slowly at ordinary temperatures, more rapidly when heated. When heated with alcohol, it yields ethylic ether and H_2SO_4 . When heated with H_2O , it yields alcohol and H_2SO_4 . It forms crystalline salts, known as **sulphovinates**, or **sulphethylates**, one of which, **sodium sulphovinate** $(\text{C}_2\text{H}_5)\text{NaSO}_4$, has been used in medicine. It is a white, deliquescent solid; soluble in H_2O .

Ethyl Sulphate— $(\text{C}_2\text{H}_5)_2\text{SO}_4$ —the true sulphuric ether, is obtained by passing vapor of SO_3 into *pure* ethylic ether, thoroughly cooled. It is a colorless, oily liquid; has a sharp, burning taste, and the odor of peppermint; sp. gr. 1.120. It cannot be distilled without decomposition. With H_2O it forms sulphovinic acid.

Sulphurous and Hyposulphurous Esters.—These compounds have recently assumed medical interest from their relationship to mercaptan, sulphonal and a number of aromatic derivatives used as medicines.

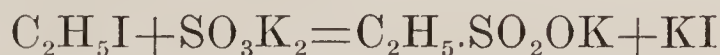
There exist two isomeric sulphurous acids (p. 89), both of which yield neutral esters, but only one of which, the unsymmetrical $\text{O} \begin{smallmatrix} \diagup \\ \text{S} \end{smallmatrix} \begin{smallmatrix} \text{H} \\ \diagdown \\ \text{OH} \end{smallmatrix}$, forms acid esters. These acid esters are known as **sulphonic acids**. (See Aromatic sulphonic acids, mercaptan, sulphones, sulphonal.)

Diethyl Sulphite— $(\text{C}_2\text{H}_5)_2\text{SO}_3$ —is produced by the action of thionyl chloride on absolute alcohol:



It is a colorless liquid, having a powerful odor: sp. gr. 1.085, boils at 161° . H_2O decomposes it into alcohol and sulphurous acid.

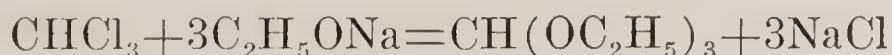
Ethyl Sulphonic Acid— $\text{SO}_2 \begin{smallmatrix} \diagup \\ \text{C}_2\text{H}_5 \\ \diagdown \\ \text{OH} \end{smallmatrix}$ —is formed by the action of ethyl iodide on potassium sulphite:



It forms salts and esters.

Sulphinic Acids—are the acid esters of hyposulphurous acid $\text{SO} \begin{smallmatrix} \text{H} \\ \diagdown \\ \text{OH} \end{smallmatrix}$, and are analogous to the sulphonic acids.

Orthoformic esters are produced by heating chloroform with sodium ethylate or by adding sodium to a mixture of chloroform, ethyl alcohol and ether:



They are colorless liquids used in certain syntheses.

Ethyl Acetate—Acetic ether— $\left. \begin{matrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_5 \end{matrix} \right\} \text{O}$ —is obtained by distilling a mixture of sodium acetate, alcohol and H_2SO_4 ; or by passing carbon dioxide through an alcoholic solution of potassium acetate:



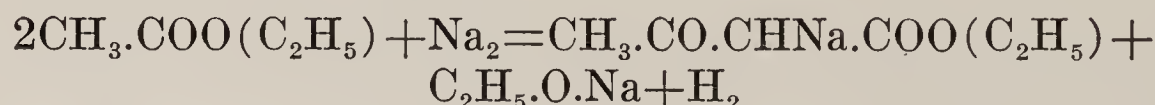
It is a colorless liquid, has an agreeable, ethereal odor: boils at 74° ; sp. gr. 0.92 at 15° ; soluble in 6 pts. water, and in all proportions in methyl and ethyl alcohols and in ether; a good solvent of essences, resins, cantharidin, morphine, gun cotton, and in general, of substances soluble in ether; burns with a yellowish-white flame. Chlorine acts energetically upon it, producing products of substitution, varying according to the intensity of the light from $\text{C}_4\text{H}_6\text{Cl}_2\text{O}_2$ to $\text{C}_4\text{Cl}_8\text{O}_2$.

Ethyl Aceto-acetate — Aceto-acetic ester — $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COO}-(\text{C}_2\text{H}_5)$ —is the most important representative of the class of β -ketonic acid esters, which are important synthetic reagents. It is prepared by dissolving 6 pts. of metallic sodium in 200 pts. of anhydrous ethyl acetate, distilling off the excess of the ester, mixing the residue with 50 per cent. acetic acid in slight excess, decanting the oil which separates, and fractioning.

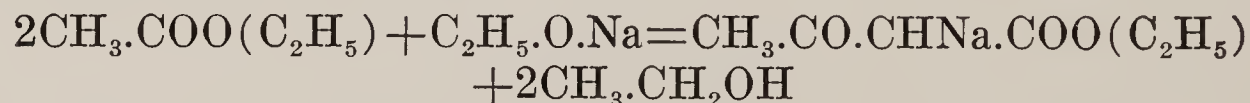
The formation of aceto-acetic ester in this process occurs in several reactions, the sum of which may be expressed by the equation:



two molecules of ethyl acetate forming one molecule of aceto-acetic ester and one of ethylic alcohol. In one stage of the reaction sodium acts upon ethyl acetate to form ethyl acetyl-sodacetate, sodium ethylate and hydrogen:



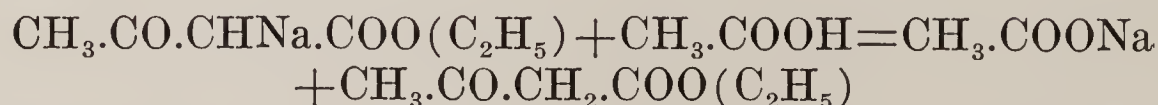
In another, sodium ethylate acts upon ethyl acetate to form ethyl acetyl-sodacetate and ethylic alcohol:



and, when the operation is properly conducted, little or no hydrogen is evolved, because that produced in the above reaction acts with sodium upon ethyl acetate to form sodium ethylate:

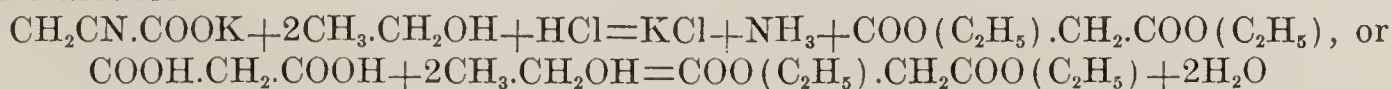


The aceto-acetic ester is liberated from its sodium derivative by acetic acid:



Aceto-acetic ester is a colorless liquid, having a pleasant odor, b. p. 181° , almost insoluble in water, and much more stable than the free acid. It is colored violet by FeCl_3 .

Malonic Ester—Neutral ethyl malonate— $\text{COO}(\text{C}_2\text{H}_5).\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5)$ —is obtained by the action of HCl upon potassium cyano-acetate, or malonic acid, and alcohol:



It is a colorless liquid, b. p. 198° , sp. gr. 1.07, insoluble in water and in alkaline solutions.

When, as in the cases of aceto-acetic and malonic esters, an ester is referred to without designation of the contained alkyl, the neutral ethyl ester is always understood.

Amyl Nitrate— $\text{C}_5\text{H}_{11}\left\{ \begin{smallmatrix} \text{NO}_2 \\ \text{O} \end{smallmatrix} \right\}$ —obtained by distilling a mixture of HNO_3 and amylic alcohol in the presence of a small quantity of urea. It is a colorless, oily liquid; sp. gr. 0.994 at 10° ; boils at 148° with partial decomposition.

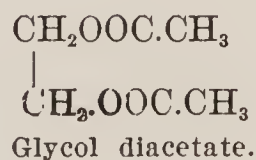
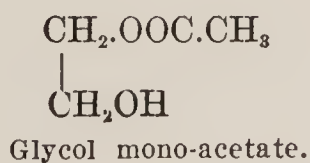
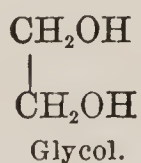
Amyl Nitrite—**Amyl nitris** (U. S. P.)— $\text{C}_5\text{H}_{11}\left\{ \begin{smallmatrix} \text{NO} \\ \text{O} \end{smallmatrix} \right\}$ —117—prepared by directing nitrous fumes into amyl alcohol, contained in a retort heated over a water-bath; purifying the distillate by washing with an alkaline solution, and rectifying.

It is a slightly yellowish liquid; sp. gr. 0.877; boils at 95° . Its vapor, which is orange-colored, explodes when heated to 260° . It is insoluble in water; soluble in alcohol in all proportions. Alcoholic solution of potash decomposes it slowly, with formation of potassium nitrite and ethyl and amyl oxides. When dropped upon fused potash, it ignites and yields potassium valerianate.

Cetyl Palmitate—**Cetin**— $\text{C}_{16}\text{H}_{31}\text{O} \left\{ \begin{smallmatrix} \text{C}_{16}\text{H}_{33} \\ \text{O} \end{smallmatrix} \right\}$ —480—is the chief constituent of **spermaceti**=**cetaceum** (U. S. P.), which, besides cetin, contains esters of palmitic, stearic, myristic, and laurostearic acids; and of the alcohols: **lethol**, $\text{C}_{12}\text{H}_{26}\text{O}$; **methol**, $\text{C}_{14}\text{H}_{30}\text{O}$; **ethol**, $\text{C}_{16}\text{H}_{34}\text{O}$, and **stethol**, $\text{C}_{18}\text{H}_{38}\text{O}$.

ESTERS OF DIHYDRIC ALCOHOLS OR GLYCOLS.

The glycols behave as diacid bases and form with the monobasic acids basic and also neutral esters:

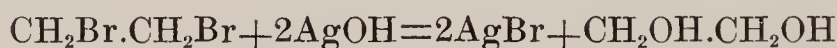


The **haloid esters** of the glycols are also basic or neutral. The basic compounds are the **glycol halohydrines**, *e.g.*, $\text{CH}_2\text{OH}.\text{CH}_2\text{Cl}$ =**Ethylene chlorhydrine**, produced by the action of the hydracids upon the glycols, or upon ethylene oxide and its homologues.

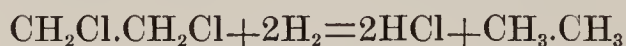
The neutral haloid esters are among the haloid derivatives of the paraffins, higher than the first. They are produced by (1) substitution of the halogen in the paraffin or in the monohalogen paraffin; thus ethyl chloride: $\text{CH}_3.\text{CH}_2\text{Cl}$ yields

ethylene chloride; $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$; (2) by addition of the halogens to the olefines, thus ethylene: $\text{CH}_2:\text{CH}_2$ yields ethylene bichloride; $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$; (3) by the action of the hydracids upon the monohalogen olefines, or upon the glycols, or upon the glycol chlorhydrines. Thus ethylene bichloride is obtained from ethylene monochloride: $\text{CHCl}:\text{CH}_2$; ethylene glycol: $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$; or ethylene chlorhydrine: $\text{CH}_2\text{OH}.\text{CH}_2\text{Cl}$. By this latter method two isomeres: $\text{CHCl}_2.\text{CH}_3$ and $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ may be produced.

The neutral haloid esters of the glycols are the starting points in the preparation of the glycols:



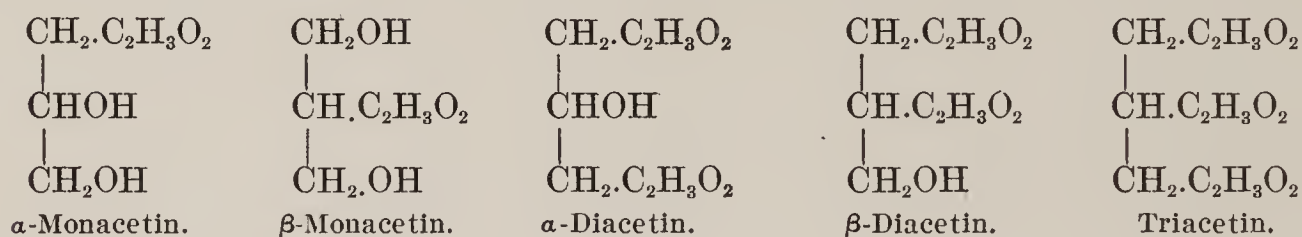
Nascent hydrogen converts them into the paraffins:



Ethylene Chloride—Elayl chloride—Dutch liquid— $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ —is obtained by passing ethylene through a retort in which chlorine is generated. It is a colorless, oily liquid, has a sweetish taste and an ethereal odor; boils at 84° . It is capable of fixing other atoms of chlorine by substitution to form a series of compounds, the most highly chlorinated of which is **carbon trichloride**, C_2Cl_6 .

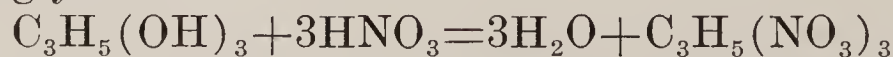
ESTERS OF THE TRIHYDRIC ALCOHOLS OR GLYCEROLS—GLYCERIDES.

The glycerols behave as triacid bases, forming three series of esters with the monobasic acids. These esters are the **mono-**, **di-**, and **triglycerides**. Moreover, as two of the hydroxyls of the alcohol are in the primary groups CH_2OH , while the third is in the secondary group, CHOH , there are two isomeres of each mono- and diglyceride:



The haloid esters are known as the **glycerol halohydrines**. Of the glycerol esters of mineral oxyacids those of nitric and phosphoric acids are of interest.

Glycerol trinitrate—Trinitroglycerol—Nitroglycerin—Glonoin— $\text{C}_3\text{H}_5(\text{NO}_3)_3$ —is formed by the action of a mixture of H_2SO_4 and HNO_3 upon glycerol:



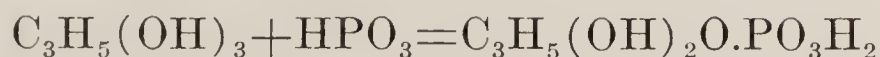
It is an odorless, yellowish oil; has a sweetish taste; sp. gr. 1.6; crystallizes in prismatic needles when kept for some time at 0° ; fuses again at 8° . When suddenly heated, or when subjected to shock it is explosively decomposed into CO_2 ; N ; H_2O and O . Alkalies saponify it to glycerol and a nitrate.

Nitroglycerol is mixed with diatomaceous earth and with other inert, absorbent substances in dynamite and in other high explosives; and, combined with nitrocellulose, it forms "smokeless powder."

It is used in medicine as a cardiac stimulant, and, in overdose, is an active poison, producing effects somewhat similar to those caused by strychnine.

Spirit of glyceryl trinitrate,—*spirit of glonoin*—*spiritus glycerylis nitratis* (U. S. P.), is an alcoholic solution of trinitroglycerol, containing 1 per cent.

Glycero-phosphoric Acid— $\text{C}_3\text{H}_5(\text{OH})_2.\text{O}.\text{PO}_3\text{H}_2$ —is the mono-glyceride of phosphoric acid. It is a product of decomposition of the lecithins, or phosphorized fats or may be formed by mixing glycerol and metaphosphoric acid:



It is a thick syrup, which is decomposed into glycerol and phosphoric acid when heated with water. It is a dibasic acid. The lithium, sodium, potassium, calcium and iron salts of this acid are occasionally used in medicine.

Glycerol Esters of Organic Acids.—The triacid glycerol esters of the acids of the acetic and acrylic series containing an even number of carbon atoms occur in the animal and vegetable fats and oils.

Tributyrin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_4\text{H}_7\text{O})_3$ —302—exists in butter. It may also be obtained by heating glycerol with butyric acid and H_2SO_4 . It is a pungent liquid, very prone to decomposition, with liberation of butyric acid.

Tricaproin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_6\text{H}_{11}\text{O})_3$ —386 — **Tricaprylin** — $\text{C}_3\text{H}_5(\text{O}.\text{C}_8\text{H}_{15}\text{O})_3$ —470—and **Tricaprin**— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{10}\text{H}_{19}\text{O})_3$ —554—exist in small quantities in milk, butter, and cocoa butter.

Tripalmitin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{16}\text{H}_{31}\text{O})_3$ —806—exists in most animal and vegetable fats, notably in palm oil. It may also be obtained by heating glycerol with 8 to 10 times its weight of palmitic acid for 8 hours at 250° . It forms crystalline plates, very sparingly soluble in alcohol, even when boiling; very soluble in ether. It fuses at 50° , and solidifies again at 46° .

Trimargarin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{17}\text{H}_{33}\text{O})_3$ —848—has probably been obtained artificially as a crystalline solid, fusible at 60° , solidifiable at 52° . The substance formerly described under this name as a constituent of animal fats is a mixture of tripalmitin and tristearin.

Tristearin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{18}\text{H}_{35}\text{O})_3$ —890—is the most abundant constituent of the solid fatty substances. It is prepared in large quantities as an industrial product in the manufacture of stearin candles, etc., but is obtained free from tripalmitin only with great difficulty.

In as pure a form as readily obtainable, it forms a hard, brittle, crystalline mass; fusible at 68° , solidifiable at 61° ; soluble in boiling alcohol, almost insoluble in cold alcohol, readily soluble in ether.

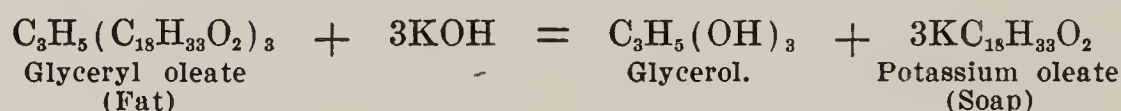
Triolein— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{18}\text{H}_{33}\text{O})_3$ —884—exists in varying quantity in all fats, and is the predominant constituent of those which are liquid

at ordinary temperatures. It may be obtained from animal fats by boiling with alcohol, filtering the solution, decanting after twenty-four hours' standing; freezing at 0° , and expressing.

It is a colorless, odorless, tasteless oil; soluble in alcohol and ether, insoluble in water; sp. gr. 0.92.

The **Neutral Oils** and **Fats** are mixtures in varying proportions of the triglycerides of the acids of the acetic and acrylic series, principally tripalmitin, tristearin, and triolein. The first two of these are solid at the ordinary temperature and the last liquid. In the oils the last predominates, in the fats the former. In the cold the oils become solid (fats), and, on heating, the fats become oils. The fats and oils are usually odorless, white or yellow, unctuous to the touch, and produce a translucent stain upon paper. They are insoluble in and lighter than water, readily soluble in ether, petroleum ether, benzene, and many other organic solvents. Although the oils do not mix with water, and promptly rise to its surface after having been agitated with it, an oil may remain suspended for a long time; suspended in very minute globules in an aqueous liquid, if bile, pancreatin, albumin, or other **emulsifying agents** be present. Such a mixture, sometimes practically permanent, is called an **emulsion**.

Like other esters the fats and oils are hydrolyzed or saponified when heated with steam or with a caustic alkali. The alcohol, glycerol, is liberated, and, if steam is used, the fatty acid also; while if an alkali is used a **soap** is formed, which is a salt of the fatty acid:



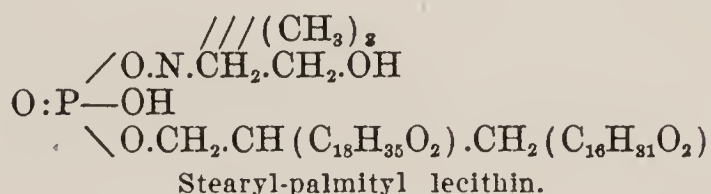
The sodium soaps are **hard**, those of potassium **soft**. **Castile soap** is a sodium soap, made from olive oil. **Yellow soap** is made from tallow or other animal fat, and contains about one-third of its weight of rosin. Lead plaster is lead soap.

The **fixed oils** are so called to distinguish them from the **volatile oils**, more properly called **essences**, which are also unctuous to the touch, and render paper translucent, but which are hydrocarbons, not esters.

The vegetable oils form three classes: (1) The **non-drying**, or **greasy oils**, which remain liquid and greasy on exposure to air. Olive oil and peanut oil are representatives of this class. (2) **Drying oils**, which dry and become hard when exposed to air. These oils, which contain linoleic acid, are used in making paints. Linseed, hemp, poppy, and sunflower oils are drying oils. (3) **Semi-drying oils** are intermediate between the other two classes, and are more or less drying. In this class are cottonseed, sesame, rape seed, and castor oils. The animal oils, used for dressing leather, as lubricants and for illumination, are fish oils, whale, and porpoise oil, neat's foot oil, lard oil, and tallow oil. **Cod liver oil** contains, besides the glycerides of oleic, myristic, palmitic, and stearic acids, small quantities of those of butyric and acetic acids. It also contains certain biliary principles, a phosphorized fat, traces of iodine and bromine, probably in organic combination, a peculiar fatty acid called **gadinic acid**, a brown substance called **gadinin**, and two alkaloidal bodies: **aselline**, $\text{C}_{25}\text{H}_{32}\text{N}_4$, and **morrhaine**, $\text{C}_{10}\text{H}_{27}\text{N}_3$. **Sperm oil** is not a true oil, but a liquid wax; it contains no glycerides, but consists mainly of esters of the higher monoatomic alcohols.

Lecithins—Phosphorized Fats.—These substances are widely distributed in animal and vegetable tissues and fluids, and are par-

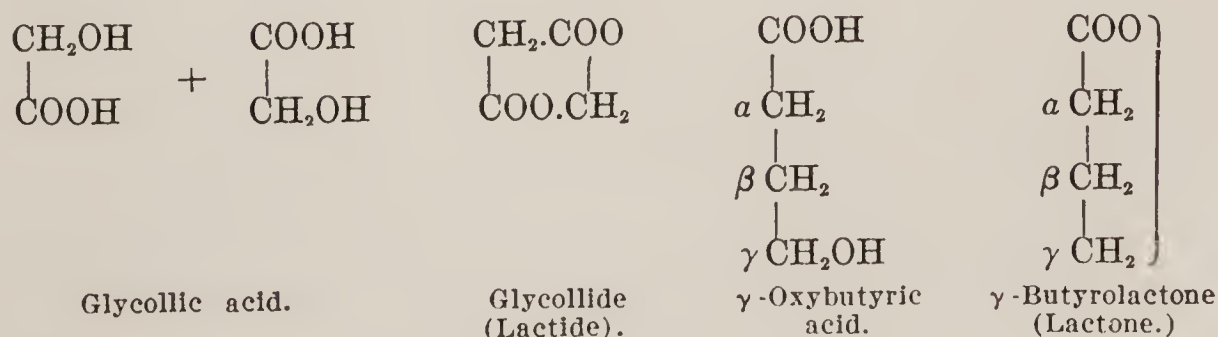
ticularly abundant in the yolks of eggs, brain, and nerve tissue, semen, and blood-corpuscles and plasma, where they probably serve as material for the formation of the more complex phosphorized bodies such as protagon and the nucleins. The lecithins are colorless or yellowish, imperfectly crystalline solids, of a waxy consistency, and very hygroscopic. They do not dissolve in water, but swell up in it like starch. They are soluble in chloroform, in benzene, and in hot alcohol and hot ether. From alcoholic solutions they crystallize in fine needles. When heated with baryta water or with acids they are decomposed into glycerophosphoric acid, chlorine, and a fatty acid, usually palmitic or stearic. The lecithins are therefore derivatives of glycerophosphoric acid, in which the two remaining hydroxyls of the glycerol are replaced by fatty acid residues, and one of the two remaining basic hydrogen atoms of the phosphoric acid is replaced by the basic radical of choline, which is a quaternary ammonium:



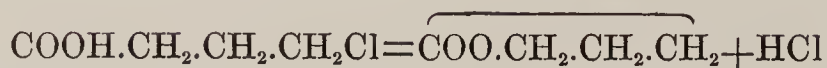
From the above formula it will be seen that the lecithins may unite with acids, through the remaining OH of the choline, or with bases, through the remaining basic H of the phosphoric acid, to form salts. The lecithins differ from each other in the nature of the fatty acids entering into their composition. Distearyl-, dioleyl- and stearyl-palmityl lecithins are known.

ESTERS OF OXYACIDS—LACTIDES AND LACTONES.

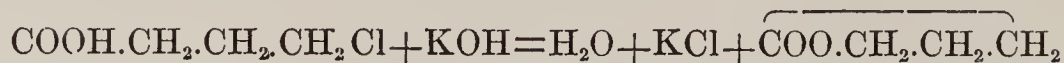
The oxyacids not only form esters with the alcohols in the same manner as the pure acids, but, being themselves both alcohol and acid, they produce cyclic esters, in the formation of which they play the part of alcohol as well as that of acid. The **lactides** are formed by the interaction of two oxyacid molecules, each performing the functions of both alcohol and acid. The **lactones**, which are formed only by the γ and higher oxyacids, are produced from a single molecule of the acid, whose carboxyl and alcoholic groups interact with each other. The following formulæ will indicate the genesis of the lactides and lactones:



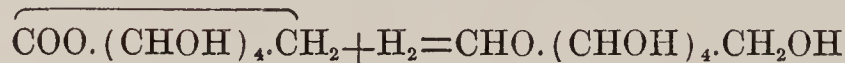
The γ lactones are formed from the γ monohalogen acids: (1) by distillation:



(2) By boiling with H_2O , KOH or K_2CO_3 :

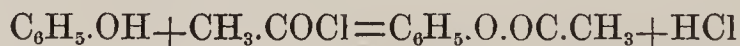


By reduction the higher lactones yield aldo-hexoses. Thus d-glucose is produced by the reduction of the lactone of d-gluconic acid:

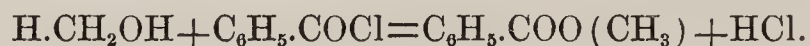


The higher oxycarboxylic acids readily lose water and are converted into lactones.

Acylation—Determination of Hydroxyl, etc.—The formation of esters by the introduction of acidyls, referred to as **acylation**, is utilized to determine the number of alcoholic or phenolic hydroxyls contained in a molecule. The acidyls usually resorted to for this purpose are acetyl, CH_3CO , and benzoyl, $\text{C}_6\text{H}_5\text{CO}$; and the reactions most frequently employed are those between the substance examined and the oxide or chloride of the acidyl. Thus phenol and acetyl chloride produce phenyl acetate:



And methyl alcohol and benzoyl chloride produce methyl benzoate:

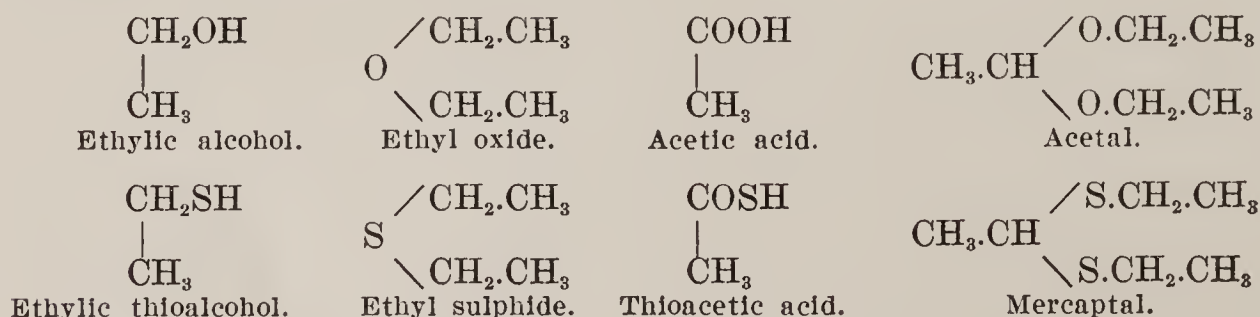


The process of **alkylation**, *i.e.*, the replacement of H in OH by alkyls to form esters, has more limited application. Alkyls may replace the H of OH in carboxyl COOH , in the methoxyl group of the primary alcohols, CH_2OH , and in the phenolic hydroxyl, $\text{C}_6\text{H}_5\text{OH}$, but not in the secondary and tertiary alcoholic groups CHOH and COH . Therefore, alkylation may sometimes be resorted to to differentiate the latter hydroxyls from the former.

SULPHUR DERIVATIVES OF THE PARAFFINS.

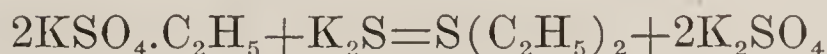
As the mineral sulphides and sulphhydrates correspond to the oxides and hydroxides, so there exist **thioethers** and **thioalcohols**, which are the counterparts of the simple ethers and of the alcohols, as well as **thioaldehydes**, **thioketones** and **thioacids**. Moreover, as sulphur may be quadrivalent or hexavalent, as well as bivalent, there exist other important compounds, the **sulphoxides**, **sulphones** and **sulphonic acids**, which have no oxygen analogues.

The following formulæ will serve to illustrate the relations of the oxygen and thio compounds:



Thioethers, or Sulphides—are produced by processes correspond-

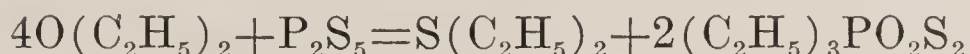
ing to those by which the ethers are formed: (1) by distilling salts of ethyl-sulphuric acids with potassium sulphide:



(2) By the action of alkyl halides upon potassium sulphide:



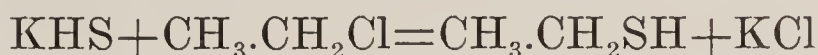
(3) By the action of phosphorus pentasulphide upon the oxygen ethers:



The last is a general method by which the thio compounds may be obtained from the corresponding oxygen compounds, the secondary products being **thiophosphoric esters**.

The thioethers are colorless liquids, insoluble in water, soluble in alcohol and ether, of disagreeable odors. They contrast with the oxygen ethers chiefly in their additive power, dependent upon the greater valence capacity of sulphur.

Thioalcohols—Mercaptans—are formed: (1) by the action of potassium sulphhydrate upon alkyl halides:

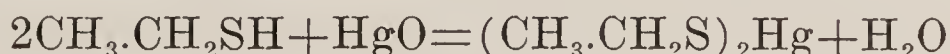


(2) By distilling the salts of the acid alkyl sulphates with potassium sulphhydrate:



(3) By the action of phosphorus pentasulphide upon the alcohol.

The thioalcohols differ in some of their general reactions from the alcohols: While the H of the OH of alcohols can only be replaced by K and Na among the metals, the H and SH may be replaced by the heavy metals as well. Thus with mercuric oxide:



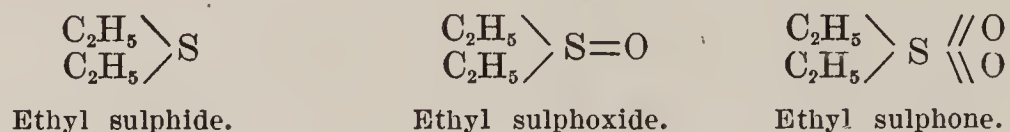
Such metallic compounds are called **mercaptids**, and the name “mercaptan” (*mercurium captans*), is due to the formation of mercury mercaptid. Owing to the greater valence capacity of sulphur, the thioalcohols do not yield thioaldehydes and thioacids on oxidation.

Ethyl mercaptan—Ethyl sulphhydrate—Thioalcohol— $\text{CH}_3 \cdot \text{CH}_2\text{SH}$ —is prepared industrially, as the first step in the formation of sulphonal, by the first of the general methods given above. It is a colorless liquid, sp. gr. 0.8325, boils at 36.2° , has an intensely disagreeable odor, burns with a blue flame, is neutral in reaction, sparingly soluble in water, soluble in alcohol and in ether, dissolves I, S and P. Potassium and sodium act upon mercaptan as they do upon alcohol, replacing the extra-radical hydrogen to produce **mercaptids**, or **thioethylates**, corresponding to the ethylates.

There also exist **mono-** and **di-thioglycols**, corresponding to the

dihydric alcohols. One of these, **monothioethylene glycol** $C_2H_4.OH.SH$, yields isethionic acid on oxidation.

Sulphoxides and **Sulphones**—are products of oxidation of the sulphides in which the sulphur is quadrivalent or hexavalent:



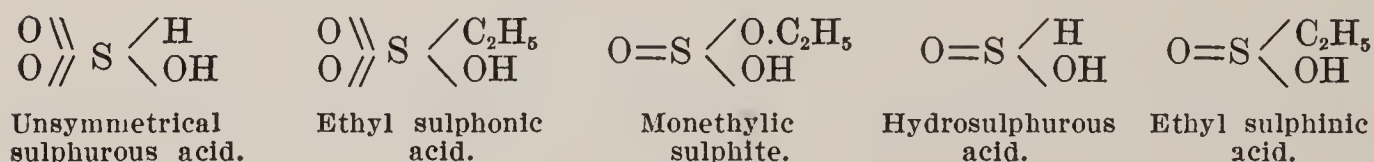
Other products of oxidation of thio-compounds, containing the group $(SO_2)''$ attached to a hydrocarbon group, are also called sulphones.

Sulphonic Acids—are acids containing the group $(O_2S.OH)'$ attached to a hydrocarbon group. The sulphonic acids of this series are formed by oxidation of the mercaptans; by the action of the paraffin iodides upon the alkaline sulphites or Ag sulphite; or by the action of sulphuric acids upon alcohols, ethers, etc. They may be considered as being derived from the unsymmetrical sulphurous acid (p. 89) by replacement of the H atom by an alkyl; and are isomeric with the monoalkyl sulphites (formula below), from which they are distinguished by the fact that the latter, being esters, are saponified by alkalies, which the former are not.

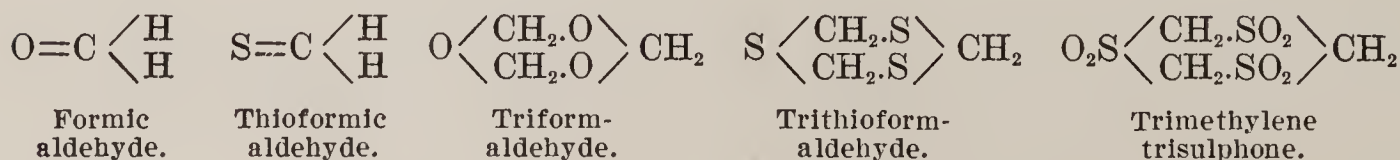
The thioglycols on oxidation also yield sulphonic acids. **Isethionic acid**, $C_2H_4.OH.SO_3H$, mentioned above, is a thick liquid, whose amido derivative is **taurin**.

In the **thiosulphonic acids**, which only exist in their salts and esters, the oxygen in the hydroxyl of the sulphonic acids is replaced by sulphur.

Sulphinic acids bear the same relation to hydrosulphurous acid that the sulphonic acids do to the unsymmetrical sulphurous acid:

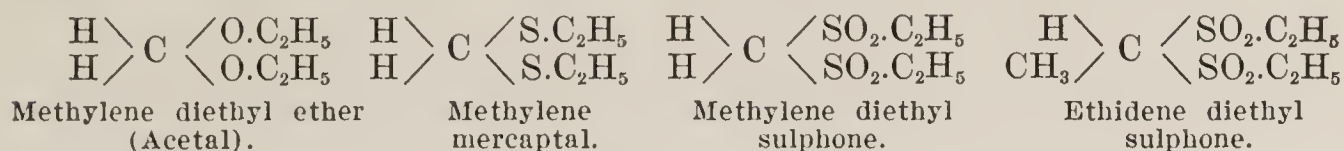


Thioaldehydes and their Sulphones.—The simple thioaldehydes are not known, owing to the tendency to polymerize which they possess to a still more marked degree than the aldehydes (p. 228). The trithioaldehydes and their sulphones are odorless, colorless solids. The relations of these compounds are shown by the formulæ:



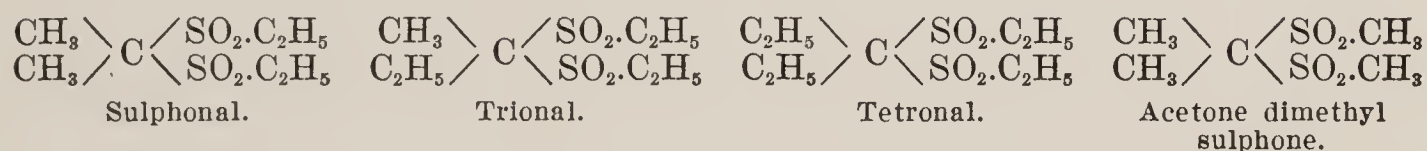
Thioacetals—Mercaptals—are produced by the action of paraffin iodides upon alkali mercaptids, or by the action of HCl upon a mix-

ture of aldehyde and mercaptan. By oxidation they yield sulphones, whose methylene hydrogen may be replaced by alkyl groups:



Sulphonal—Acetone Diethyl Sulphone—Disulphethyl-dimethylmethane — $(\text{CH}_3)_2:\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$ — is obtained by oxidizing ethyl mercaptol by potassium permanganate. It crystallizes in thick, colorless prisms, difficultly soluble in cold water or alcohol, readily soluble in hot water or alcohol, and in ether, benzene and chloroform. It fuses at 126° and boils at 300° , suffering partial decomposition.

Sulphonal contains two ethyl groups, **trional** contains three, and **tetronal** four. Their hypnotic power increases with the number of ethyl groups which they contain. Other "sulphonals" are obtainable from the corresponding mercaptols by methods similar to the above. Among these is **acetone dimethyl sulphone**, which contains no ethyl group, and has no hypnotic action. The relations of these compounds is shown by the following formulæ:



Ichthyol—is the Na salt of a complex sulphonic acid, having the empirical formula $\text{C}_{28}\text{H}_{36}\text{S}_3\text{O}_6\text{Na}_2$, obtained by the distillation and purification of an ozocerite (a mineral pitch). It is a dark brown, pitchlike mass, having a disagreeable odor, soluble in water and in glycerol.

Thioacids and their Thioanhydrides.—In the thioacids of the acetic series the sulphur is substituted for the oxygen in the hydroxyl. **Thioacetic acid**, $\text{CH}_3.\text{CO}.\text{SH}$, is formed by the action of phosphorus pentasulphide upon acetic acid.

Carbon Disulphide— CS_2 —bears the same relation to sulphotothiocarbonic acid, $\text{CS} \begin{smallmatrix} \text{SH} \\ \text{OH} \end{smallmatrix}$, and to trithiocarbonic acid, $\text{CS} \begin{smallmatrix} \text{SH} \\ \text{SH} \end{smallmatrix}$, that carbon dioxide bears to carbonic acid. It is prepared by passing vapor of S over C heated to redness, is partly purified by rectification, and obtained pure by redistillation over mercuric chloride.

It is a colorless liquid. When pure it has a peculiar, but not disagreeable odor, the nauseating odor of the commercial product being due to the presence of another sulphurated body; boils at 47° ; sp. gr. 1.293; very volatile. Its rapid evaporation in vacuo produces a cold of -60° . It does not mix with H_2O . It refracts light strongly.

It is highly inflammable, and burns with a bluish flame, giving off CO_2 and SO_2 ; its vapor forms highly explosive mixtures with air,

which detonate on contact with a glass rod heated to 250° . Its vapor forms a mixture with nitrogen dioxide, which when ignited, burns with a brilliant flame, rich in actinic rays.

A substance also exists, intermediate in composition between CO_2 and CS_2 , known as **carbon oxysulphide**, CSO , which is an inflammable, colorless gas, obtained by decomposing potassium thiocyanate with dilute H_2SO_4 .

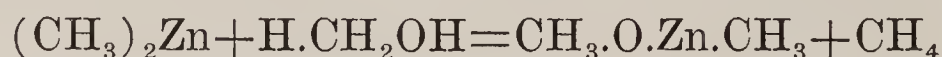
Toxicology.—Workmen engaged in the manufacture of CS_2 , and in the vulcanization of rubber, as well as others exposed to the vapor of the disulphide, are subject to a form of chronic poisoning which may be divided into two stages. The first, or stage of excitation, is marked by headache, vertigo, a disagreeable taste, and cramps in the legs. The patient talks, laughs, sings, and weeps immoderately, and sometimes becomes violently delirious. In the second stage the patient becomes sad and sleepy, sensibility diminishes, sometimes to the extent of complete anesthesia, especially of the lower extremities, the headache becomes more intense, the appetite is greatly impaired, and there is general weakness of the limbs, which terminates in paralysis.

The only remedy which has been suggested is thorough ventilation of the workshop, and abandonment of the trade at the first appearance of the symptoms.

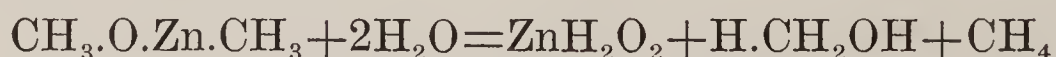
ORGANO-METALLIC COMPOUNDS.

These are compounds of organic radicals with metallic elements, the best known being those of the alkyls with zinc and mercury.

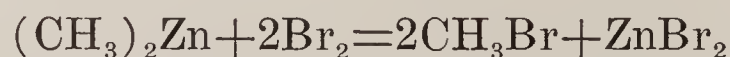
Zinc-methyl, or **Zinc Methide**— $(\text{CH}_3)_2\text{Zn}$, and **Zinc-ethyl**, or **Zinc Ethide**— $(\text{C}_2\text{H}_5)_2\text{Zn}$ —are formed by heating to 130° – 150° methyl or ethyl iodide with excess of zinc amalgam, and distilling without contact of air. They are colorless liquids, the former b. p. 46° , sp. gr. 1.386, the latter b. p. 118° , sp. gr. 1.182. On contact of air they ignite and burn, giving off dense clouds of ZnO . By the moderated action of air they produce solid oxyalkylates: $\text{Zn} \begin{smallmatrix} \text{CH}_3 \\ \diagdown \\ \text{O} \cdot \text{CH}_3 \end{smallmatrix}$, or alcoholates: $\text{Zn} \begin{smallmatrix} \text{O} \cdot \text{CH}_3 \\ \diagdown \\ \text{O} \cdot \text{CH}_3 \end{smallmatrix}$. The former are also produced, along with hydrocarbons, by the action of zinc-alkyls upon alcohols:



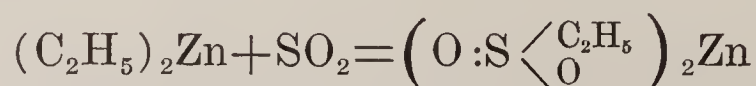
and are decomposed by water with formation of hydrocarbons and primary alcohols:



With the halogens the zinc alkyls react violently to form alkyl halides:



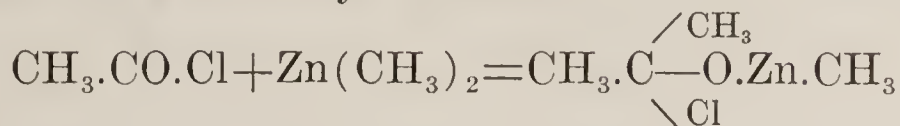
They unite with sulphur dioxide to produce zinc alkyl-sulphinates (p. 286):



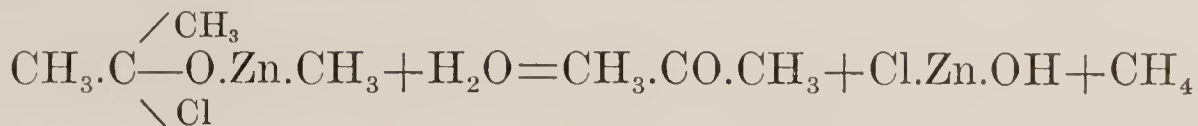
With acidyl chlorides and aldehydes they form complex com-

pounds, which are decomposed by water to form ketones, or tertiary or secondary alcohols.

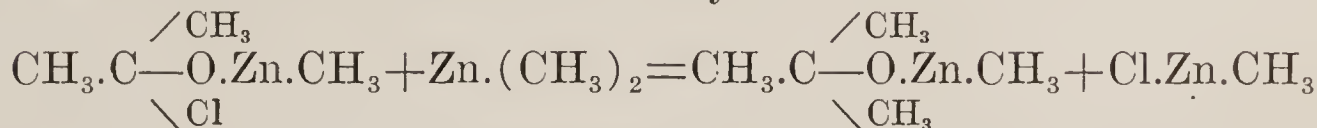
Zinc alkyls act with acidyl chlorides to form addition products:



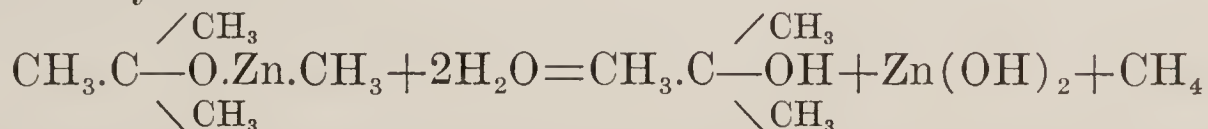
which are decomposed by H_2O with formation of ketones and hydrocarbons:



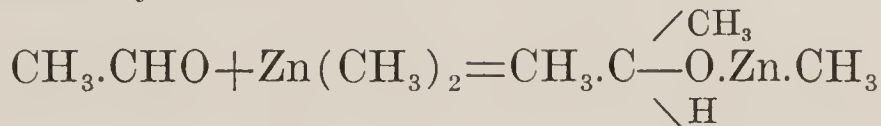
or in which the Cl atom may be replaced by an alkyl by the action of a second molecule of the zinc alkyl:



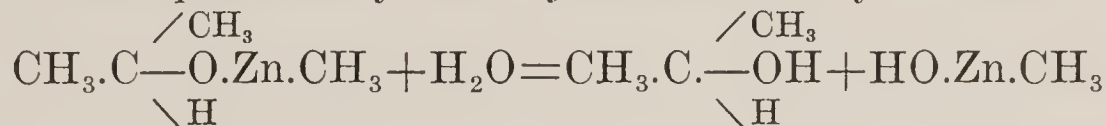
and this compound on decomposition by H_2O yields a tertiary alcohol and a hydrocarbon:



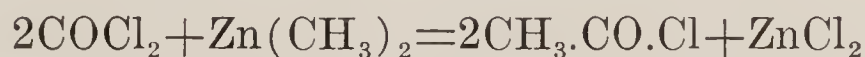
By its action upon aldehydes the zinc alkyl forms addition products similar to those produced with the acidyl halides, the halogen being, however, replaced by H:



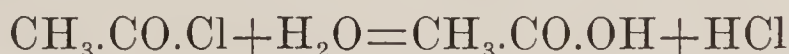
which on decomposition by water yields secondary alcohols:



Carbonyl chloride reacts with the zinc alkyl to form acidyl chlorides:



which with water produces the corresponding acids:

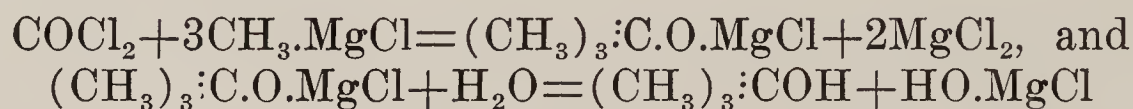


Organo-Magnesium Compounds.—Compounds corresponding to the zinc alkyls: R_2Mg are known, and are equally unstable and difficult to handle. The mixed organo-halide compounds of Grignard of the type $\text{R}.\text{Mg}.\text{X}$, in which R is a univalent hydrocarbon radical, aliphatic or cyclic, and X a halogen, are more convenient to handle and give better results in the syntheses of hydrocarbons, alcohols and monobasic acids (pp. 203, 212, 251). Magnesium turnings in the presence of anhydrous ether react with alkyl bromides and iodides to form gray semi-crystalline compounds which are etherates of alkyl magnesium halides, "oxonium" compounds, in which the

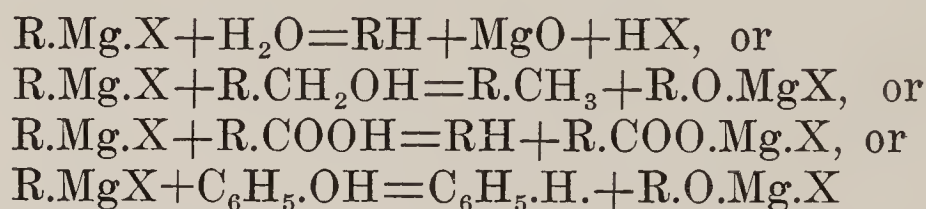
oxygen is quadrivalent and basic, of the type $\begin{array}{c} \text{R} \backslash \quad / \text{X} \\ \text{O} \\ \text{R} / \quad \backslash \text{MgR}' \end{array}$, in which

R. R. are the alkyls of the ether, R' that of the alkyl halide, and X the halogen. These in turn are decomposed with the formation of alkyl magnesium halides of the type: R.Mg.X. Or the reaction may take place in two stages: $R'X + R_2O = \begin{matrix} R \backslash & / R' \\ O & \\ R / & \backslash X \end{matrix}$, and $\begin{matrix} R \backslash & / R' \\ O & \\ R / & \backslash X \end{matrix} + Mg = R'.Mg.X + R_2O$, the ether behaving as a catalyser. The reaction does not occur in the simple form: $R'X + Mg = R'.Mg.X$, as it does not occur in the absence of ether, as when benzene, petroleum ether, etc. are used as solvents.

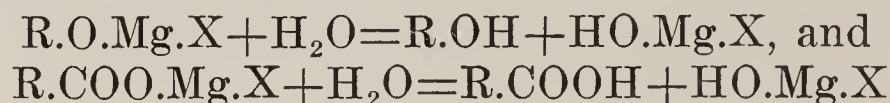
Carbonyl chloride and alkyl magnesium halides interact to produce tertiary alcohols:



Water and compounds containing hydroxyls, such as alcohols, acids, phenols, etc., decompose the organo-halide magnesium compounds with formation of the corresponding hydrocarbons, according to the equations:

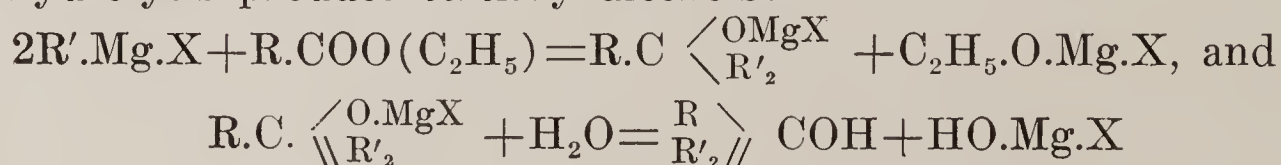


The compounds R.O.Mg.X and R.COO.Mg.X are themselves hydrolyzed by water with regeneration of the corresponding alcohol or acid:

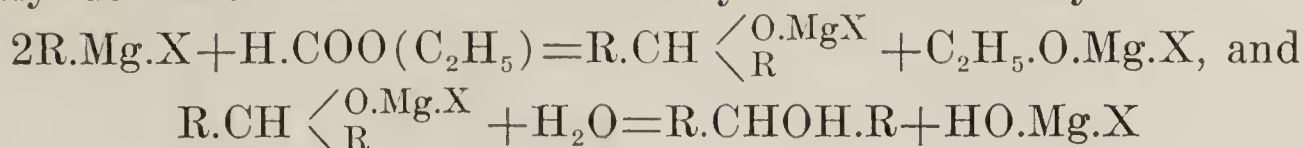


The alkyl magnesium compounds act upon substances, such as aldehydes and ketones, containing an oxygen atom doubly linked to carbon, to form condensation products of the types R.O.Mg.X or R.CH.R.O.Mg.X. These condensed compounds are readily hydrolyzed by dilute acids to magnesium hydrohalides, and a hydroxyl is attached to the carbon in the position of the oxygen linkage. The above, known as the *Grignard reactions*, are extensively used in the preparation of alcohols, both aliphatic and cyclic. The reaction with formic aldehyde differs from that with its superior homologues. The phenyl magnesium halides are readily oxidized by the passage of air through their ethereal solutions with formation of condensed compounds of the type R.O.Mg.X which when hydrated yield phenols.

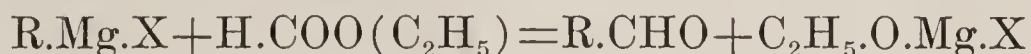
The organo-magnesium halides react with esters of monobasic acids, except formic, with the formation of condensed products which on hydrolysis produce tertiary alcohols:



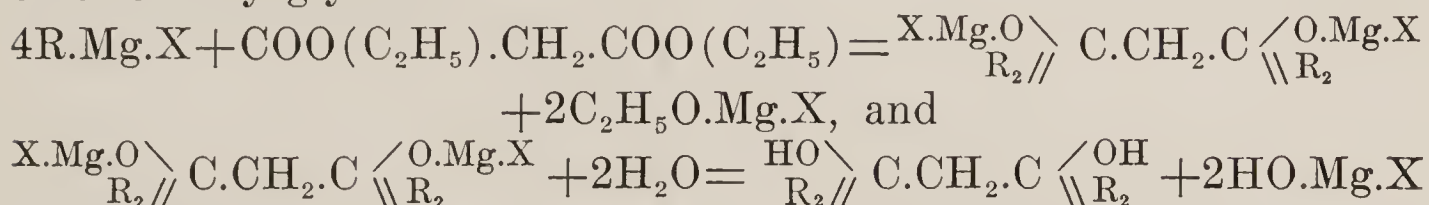
Ethyl formate under like conditions yields a secondary alcohol:



By operating at -50° a reaction is obtained between equal molecules with formation of an aldehyde:



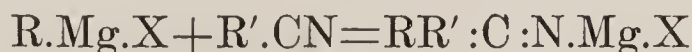
The esters of dibasic acids behave in the same manner with formation of ditertiary glycols:



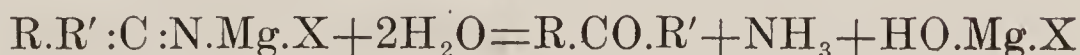
By passing CO_2 through solutions of the alkyl magnesium halides, compounds of the type R.COO.MgX are precipitated, which when hydrolyzed at low temperatures produce monobasic acids (p. 251). But with phenyl magnesium halides, the principal final products are alcohols.

The reactions between acidyl chlorides or anhydrides and alkyl magnesium halides are violent. When moderated by ice they result in the formation of tertiary alcohols (p. 213).

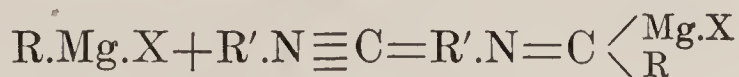
The organo-magnesium halides condense with nitriles according to the equation:



and the products produce ketones by hydrolysis:



But with isonitriles condensed products are formed:



which when hydrolyzed produce imines:



Alkyl magnesium halides act upon amides to produce aldehydes or ketones (pp. 227, 234).

Grignard's compounds react with ammonia, amines (including aniline) and phenyl hydrazine with the formation of a hydrocarbon and of compounds of the types: $\text{H}_2\text{N.Mg.X}$; R.HN.Mg.X ; R.R'.N.Mg.X ; $\text{C}_6\text{H}_5.\text{N}(\text{MgX}).\text{NH}(\text{MgX})$, which are known as *Meunier's compounds*.

NITROGEN DERIVATIVES OF THE PARAFFINS.

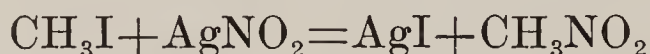
Speaking strictly, the only nitrogen derivatives of the paraffins are the nitriles, derived from the paraffins by substitution of N for H_3 , as $\text{CH}_3.\text{CN}$, from $\text{CH}_3.\text{CH}_3$ and the diazo paraffins, $(\text{N}_2)''\text{CH.CH}_3$,

but the compounds derivable from the paraffins and from their oxidation products by substitution of nitrogen containing groups, NO_2 , NO , NH_2 , NH , NOH , —N:N— , and =N.N= , are numerous, varied and important.

NITROPARAFFINS.

The univalent group (NO_2) is designated by the syllable **nitro** in the names of compounds containing it.

The **mononitroparaffins**—isomeric with the nitrous esters are derived from the paraffins by the substitution of NO_2 for an atom of hydrogen, and are distinguished as *primary*, *secondary* and *tertiary*, in the same manner as the corresponding alcohols, according as the NO_2 is united to CH_2 (CH_3 in nitromethane), or CH , or C . They are formed by the action of the alkyl iodides upon silver nitrite:

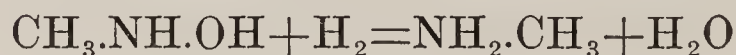


They are isomeric with the nitrous esters: $\text{CH}_3.\text{CH}_2.\text{N} \begin{smallmatrix} // \\ \backslash \end{smallmatrix} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} = \text{mono-nitroethane}$, and $\text{CH}_3.\text{CH}_2.\text{ON}:\text{O} = \text{Ethyl nitrite}$. These isomeres may be distinguished by the action of KOH , which saponifies the esters:



but has no action upon the nitroparaffins.

Nascent hydrogen converts them first into hydroxylamine compounds: $\text{CH}_3.\text{NO}_2 + 2\text{H}_2 = \text{CH}_3.\text{NH.OH} + \text{H}_2\text{O}$, which are in turn further reduced to monamines, or amidoparaffins:



AMINES AND AMMONIUM DERIVATIVES.

The amines are compounds derived from ammonia by the substitution of hydrocarbon (non-acid) radicals for a part or all of its hydrogen.

They are classified into **monamines**, derived from a single molecule of ammonia, **diamines**, derived from two such molecules, and **triamines**, derived from three.

MONAMINES AND THEIR DERIVATIVES.

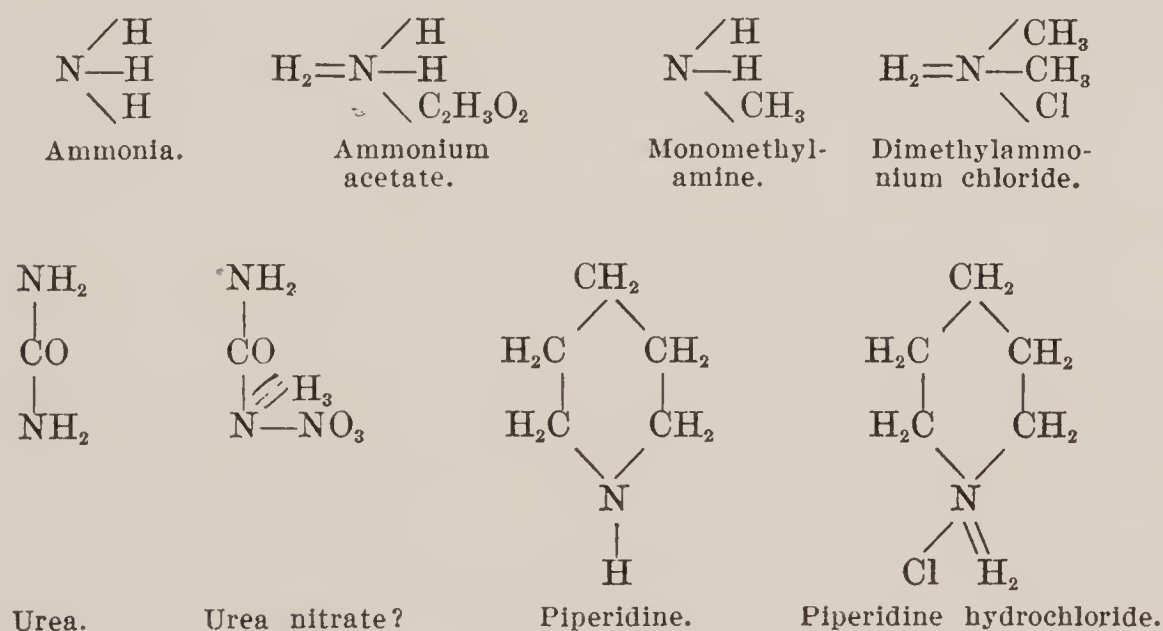
The monamines are **primary**, **secondary**, or **tertiary**, as one, two, or three of the hydrogen atoms of ammonia have been replaced. They are also distinguished as **amine**, **imine**, and **nitrile bases**. When, in secondary or tertiary amines, the substituted radicals are alike the amines are designated as **simple**, when the radicals are different the amines are **mixed**. The primary monamines, containing the group NH_2 , are **amido-paraffins**; while the secondary, containing the group

NH, are imido-paraffins. The monamines have the algebraic formula, $\text{NC}_n\text{H}_{2n+3}$

A nomenclature similar to the above is also used in speaking of nitrogen in other, more complex, organic compounds. It is said to be in **primary combination**, or as **amide**, or **amine nitrogen**, when in the **amido**, or **amino group** $(\text{NH}_2)'$, in **secondary combination**, or as **imide**, or **imine nitrogen**, when in the **imido**, or **imine, group** $(\text{NH})''$, and in **tertiary combination**, or as **nitrile nitrogen**, when in the form N''' . **Azo-**, **diazo-**, and **hydrazo-** nitrogen is in the forms $-\text{N}:\text{N}-$ and $=\text{N.N}=-$.

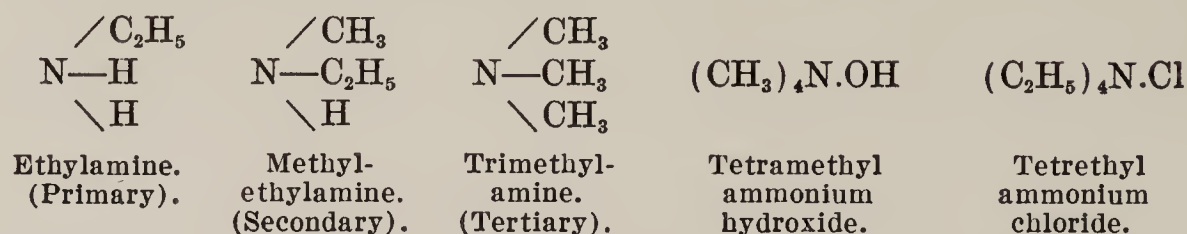
The monamines are sometimes called **compound ammonias**, from their resemblance to ammonia in their chemical properties, as well as from their origin. They combine with water to produce **quaternary ammonium hydroxides**, similar in constitution, alkalinity, and basicity to ammonium hydroxide; and with acids, without elimination of hydrogen, to form salts, similar to the ammoniacal salts.

The aliphatic monamines are the most simply constituted of a great variety of nitrogen derivatives, including the primary monamides, the diamides, such as urea, and the vegetable alkaloids, which have this in common with the amines, that they are basic in character, and in combining with acids, form salts in the same manner as ammonia does, *i.e.*, by change of the nitrogen valence from three to five, and, consequently, without elimination of hydrogen; thus:

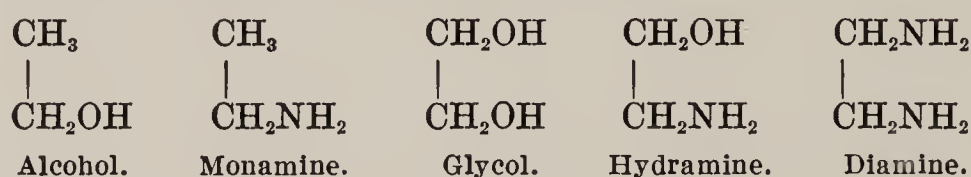


The naming of these compounds has been the subject of much discussion. As the substances formed by the union of ammonia with acids are regarded as salts of ammonium, not of ammonia, so these compounds are not salts of urea, piperidine, morphine, etc., but salts of hypothetical bases, containing a quinivalent nitrogen atom, which in the free base is trivalent. The names: *ureium nitrate*, *piperidium chloride*, *morphium sulphate*, etc., are therefore the analogues of *ammonium acetate* and *dimethylammonium chloride*. For the chlorine, bromine, and iodine compounds the names: piperidine hydrochloride, morphine hydrobromide, quinine hydroiodide, etc., may be conveniently retained, they being regarded as the free bases, plus hydrogen, plus the halogen.

The following formulæ indicate the constitution of the amines and their hydroxides and salts:



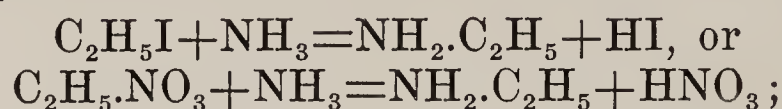
The primary monamines, the hydramines, and the diamines may also be considered as derived from the monohydric and dihydric alcohols by substitution of NH_2 for OH .



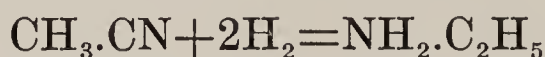
The **primary monamines** are formed: (1) by distilling the isocyanic esters with caustic potash:



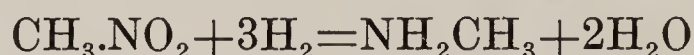
(2) By heating the alkyl iodides, or the nitric esters with alcoholic ammonia:



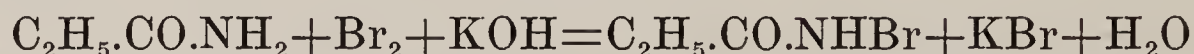
(3) By the action of nascent H in alcoholic solution upon the nitriles:



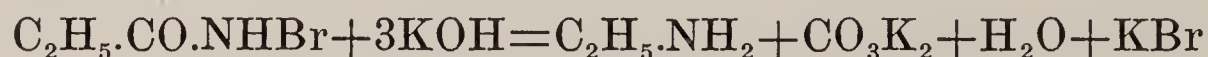
(4) By the action of nascent H upon the nitroparaffins:



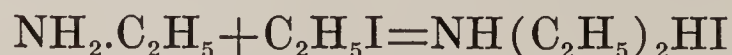
(5) From the monamides of the fatty series monoamines, containing one atom of carbon less than the amide, are formed by the action of bromine and potassium hydroxide. The reaction occurs in two stages. First a bromide is produced:



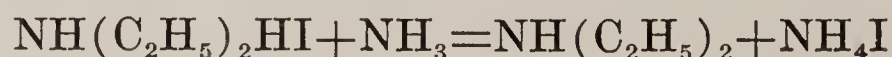
which is in turn converted into the amine with loss of the carbonyl group:



The **secondary monamines** are formed, as intermediate products, by the action of the alkyl iodides upon the primary monamines in the presence of excess of ammonia. The alkyl-ammonium iodide is first produced:



and this reacts with the ammonia:



The final products of the reaction are the tetrammonium iodides: $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$.

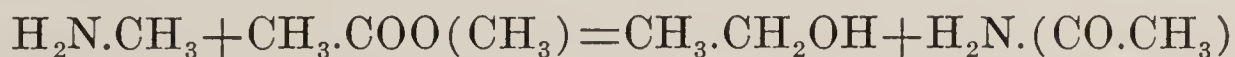
The **tertiary monamines** are obtained by the dry distillation of the quaternary ammonium hydroxides, iodides, or chlorides:



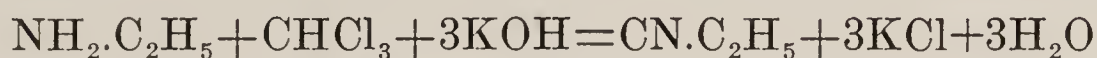
or by heating the primary or secondary amines with excess of potassium alkyl sulphate:



The primary and secondary amines react with esters of the monocarboxylic acids to form alcohols and primary or secondary amides. Thus methylamine and methyl acetate produce ethyl alcohol and acetamide:



The primary monamines, when warmed with chloroform and alcoholic potash, yield **carbylamines**, **isocyanides**, or **isonitriles**:



(See Chloroform, test 1, p. 206.)

When ethereal solutions of primary monamines and of carbon disulphide are evaporated, a residue is obtained which, when heated in aqueous solution with AgNO_3 , or FeCl_3 , or HgCl_2 forms a sulphide of the metal and a "mustard oil," having a pungent odor. This is Hoffman's test for primary monamines.

Methylamine— $\text{H}_2\text{N}.\text{CH}_3$ —is a colorless, inflammable gas, having a fishy, ammoniacal odor. Very soluble in water (1,154 volumes in one at 12.5°), forming a highly caustic and alkaline solution. It neutralizes acids with formation of methyl ammonium salts, which are soluble in water.

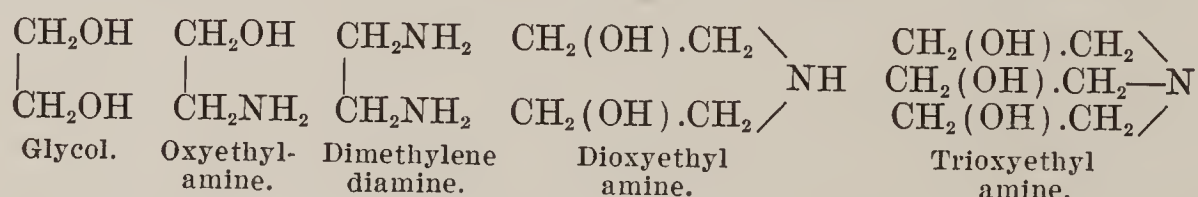
Dimethylamine— $\text{HN}(\text{CH}_3)_2$ —is a liquid below 7.2° , has an ammoniacal odor, and is very soluble in water. Its chloroplatinate forms yellow needles.

Trimethylamine— $\text{N}(\text{CH}_3)_3$ —is formed by the action of methyl iodide upon NH_3 , and as a product of decomposition of many organic substances. It occurs naturally in combination in cod-liver oil, ergot, chenopodium, yeast, guano, and many flowers. It is an oily liquid below 9° , having a fishy odor, alkaline, soluble in water, alcohol and ether.

Tetramethyl-ammonium Hydroxide— $\text{HO.N}(\text{CH}_3)_4$ —is a **quaternary ammonium hydroxide**, corresponding to ammonium hydroxide, and is obtained by decomposing the iodide, $\text{IN}(\text{CH}_3)_4$, which is formed by the action of methyl iodide upon trimethylamine. It is a crystalline, deliquescent, caustic solid, not volatile without decomposition. Like other carbon-nitrogen hydroxides and hydramines, it absorbs carbon dioxide from the air.

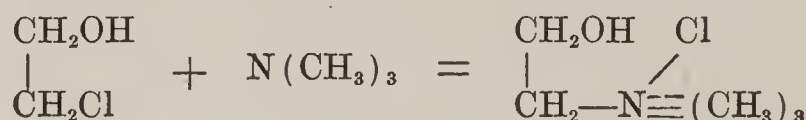
OXYAMINES (HYDRAMINES), DIAMINES

The primary monamines may be considered as being derived from the monoatomic alcohols by the substitution of the amido group, NH_2 , for the hydroxyl. From the dihydric alcohols, the glycols, two classes of amido compounds may be similarly derived. One of these, the **oxyamines**, **hydroxamines**, or **hydramines**, contain a single amido group, and retain an alcoholic hydroxyl. In the **diamines** both hydroxyls are replaced by amido groups. The oxyamines are primary, secondary and tertiary in the same manner as the monamines:



Aldehyde-ammonia (p. 319), a crystalline solid formed by the action of dry NH_3 on acetic aldehyde: $\text{CH}_3\cdot\text{CHO} + \text{NH}_3 = \text{CH}_3\cdot\text{CH} \begin{array}{l} \text{OH} \\ \text{NH}_2 \end{array}$ may be considered as **ethidene hydroxylamine** in which both OH and NH_2 are attached to the same carbon atoms.

Choline—*Trimethyloxethylammonium hydroxide* — *Bilineurine*— $\begin{array}{c} \text{CH}_2\text{OH} \quad \text{OH} \\ | \quad \diagup \\ \text{CH}_2\cdot\text{N}\equiv(\text{CH}_3)_3 \end{array}$ —occurs in hops, in fungi, in certain seeds, in the human placenta, in bile, in the yolks of eggs, and in the cerebro-spinal fluid in epilepsy and other organic diseases of the nervous system. It is a constituent of the lecithins. It is formed synthetically (as its chloride) by the union of ethylene chlorhydrine and trimethylamine:



It is produced during the first forty-eight hours of putrefaction of animal tissues, from the decomposition of the lecithins, and diminishes from the third day, when other ptomaines (neuridine, putrescine, cadaverine) increase in amount. When heated, it splits up into glycol and trimethylamine. Nitric acid converts it into muscarine.

It is a thick syrup, soluble in H_2O and in alcohol, and strongly alkaline in reaction. Even in dilute aqueous solution it prevents the coagulation of albumin and redissolves coagulated albumin and fibrin. It is a strong base; attracts CO_2 from the air; forms with HCl a salt, soluble in alcohol, which crystallizes in plates and needles, resembling those of cholesterin. Its chloroplatinate is purified with difficulty; its chloroaurate readily. It is poisonous only in large doses.

Amanitine—*Trimethyloxethylideneammonium hydroxide*—*Isocho-*
 $\begin{array}{c} \text{CH}_3 \quad \text{OH} \\ | \quad \diagup \\ \text{CHOH}\cdot\text{N}\equiv(\text{CH}_3)_3 \end{array}$ —is an isomere of choline, existing along with

muscarine in *Agaricus muscarius*. It is produced by methylation of aldehydeammonia: $\text{CH}_3\cdot\text{CHOH}\cdot\text{NH}_2$. By oxidation with HNO_3 it yields muscarine.

Muscarine.— $\begin{array}{c} \text{CH}_2\text{OH} \quad \text{OH} \\ | \quad \diagup \\ \text{CHOH}\cdot\text{N}\equiv(\text{CH}_3)_3 \end{array}$ —is related to choline, neurine and amanitine from which it may be obtained by oxidation.

It occurs in nature in *Agaricus muscarius*, and is produced during putrefactive decomposition of proteins.

The free base occurs in very deliquescent, irregular crystals, or, if not perfectly dry, a colorless, odorless, and tasteless, but strongly alkaline syrup; readily soluble in all proportions in water and in alcohol; very sparingly soluble in chloroform; insoluble in ether. It is a more powerful base than ammonium hydroxide. When decomposed it yields trimethylamine. Its chloroplatinate crystallizes in octahedra. Its chloride forms colorless, brilliant, deliquescent needles.

When administered to animals, muscarine causes increased secretion of saliva and tears; vomiting; evacuation of feces, at first solid, later liquid; contraction of the pupils, almost to the extent of closure; diminution of the rapidity of the pulse; interference with respiration and locomotion; gradual sinking of the heart's action and respiration; and death. Atropine prevents the action of muscarine and diminishes its intensity when already established.

Neurine—Trimethylvinylammonium hydroxide— $\begin{array}{c} \text{CH}_2 \quad \text{OH} \\ || \quad \diagup \\ \text{CH}\cdot\text{N}\equiv(\text{CH}_3)_3 \end{array}$ —is a base resembling choline, for which reason it is considered here, although its proper place is as a derivative of vinylamine. It has been obtained from brain tissue and from the suprarenal capsule, probably as a product of decomposition of protagon. It is produced from choline by boiling with baryta water. The same body is one of the alkaloids produced by the putrefaction of muscular tissue, and is endowed with poisonous qualities, resembling, but less intense than, those of muscarine.

Betaines—are lactams (p. 323) of hypothetical substances, such as that which would be derived from choline: $\begin{array}{c} \text{CH}_2\text{OH} \\ | \quad \diagup \text{OH} \\ \text{CH}_2\cdot\text{N}\equiv(\text{CH}_3)_3 \end{array}$ by oxidation of the methoxyl group to a carboxyl: $\begin{array}{c} \text{COOH} \\ | \quad \diagup \text{OH} \\ \text{CH}_2\cdot\text{N}\equiv(\text{CH}_3)_3 \end{array}$. Although this substance, containing both carboxyl and basic hydroxyl, is unknown, the corresponding betaine aldehyde and chloride are known (see formulæ below).

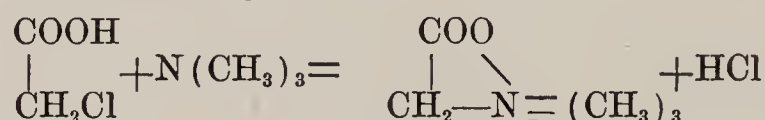
The betaines have the general formula: $\begin{array}{c} \text{COOH} \quad \text{OH} \\ | \quad \diagup \\ \text{R}''\text{—N}\equiv \end{array}$, in which R'' may be any bivalent hydrocarbon radical, and in which the three

remaining nitrogen valences may be satisfied by univalent radicals or by a trivalent radical. Or the arrangement of the valences may

be reversed, as in nicotic-methyl betaine: $\begin{array}{c} \text{COO} \text{---} \\ | \\ (\text{C}_5\text{H}_4)''' \equiv \text{N} \text{---} \text{CH}_3. \end{array}$

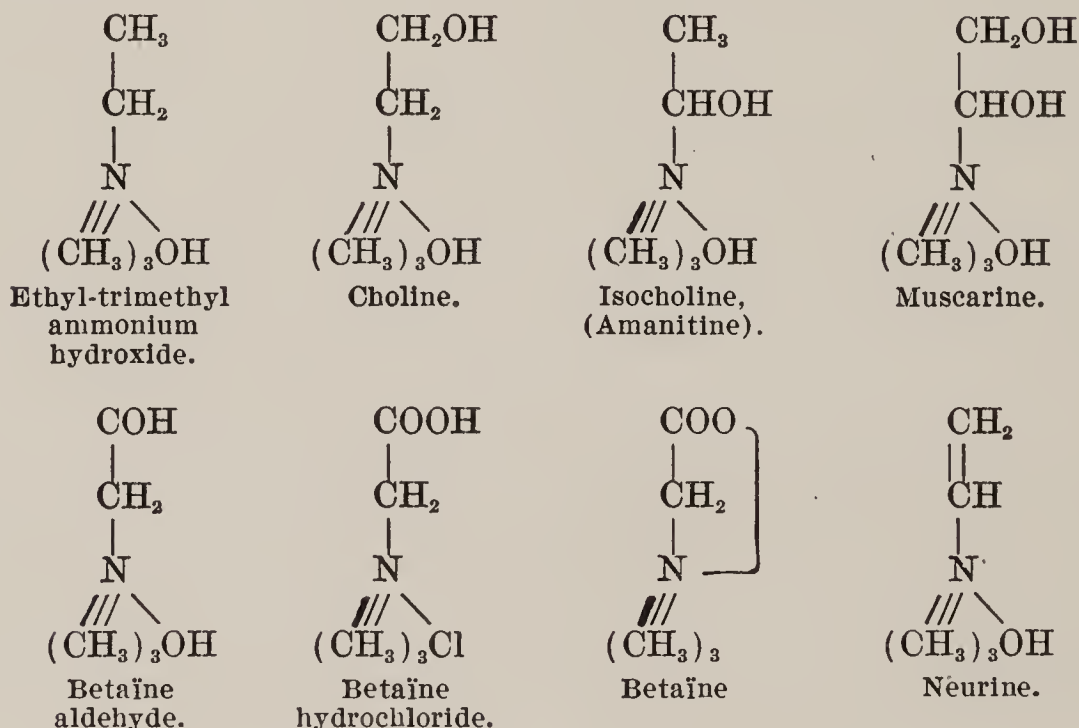
Betaine—*Trimethyl-acetic betaine* — *Oxyneurine* — *Oxycholine*—*Trimethyl-glycocoll*— $\begin{array}{c} \text{COO} \\ | \quad \backslash \\ \text{CH}_2 \text{---} \text{N} \equiv (\text{CH}_3)_3 \end{array}$ —was first obtained from beet-juice (*Beta vulgaris*). It exists in beet-sugar molasses, in cotton-seed, and in malt. It is formed by several synthetic methods, *e.g.*, by the action of methyl iodide upon amido-acetic acid (p. 323):

$\begin{array}{c} \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{NH}_3 \end{array} + 3\text{CH}_3\text{I} = 3\text{HI} + \begin{array}{c} \text{COO} \\ | \quad \backslash \\ \text{CH}_2 \text{---} \text{N} \equiv (\text{CH}_3)_3 \end{array}$; or by the interaction of mono-chloroacetic acid and trimethylamine:

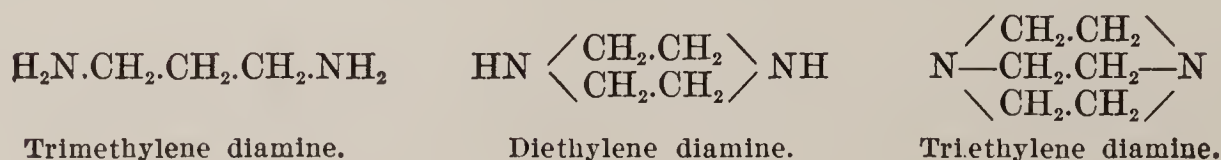


Betaine crystallizes in large, deliquescent crystals, with one molecule of water of crystallization, very soluble in water and in alcohol. It is decomposed by heat with evolution of trimethylamine, a fact which is utilized to obtain that substance from beet-molasses. It is strongly basic and forms crystalline salts. Its chloraurate is crystalline and very sparingly soluble in cold water.

The relations of the oxyamine bases are shown in the following formulæ:



Diamines—are primary, secondary, and tertiary, as they contain two groups NH_2 , or two groups NH , or two N atoms:



The primary diamines only are acyclic compounds. They have the algebraic formula: $N_2C_nH_{2n+4}$; the secondary, $N_2C_nH_{2n+2}$; and the tertiary, $N_2C_nH_{2n}$. The secondary and tertiary diamines are not known beyond the ethylene compounds and are cyclic compounds (see Piperazine).

The primary diamines are obtained (1) by the reduction of the olefine dicyanides. Thus ethylene cyanide yields tetramethylene diamine:



(2) As hydrobromides, by heating the olefine bromides with alcoholic ammonia to 100° under pressure:



(3) By reduction of the dinitroparaffins:



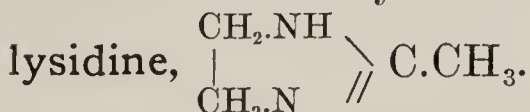
(4) By elimination of CO_2 from the diamido acids by bacterial action.

Alkyls or acidyls may be substituted for H in NH_2 of the diamines, as in the monamines (p. 294). The formation of their dibenzoyl derivatives: $(C_6H_5.CO).HN.(CH_2)_4.NH.(CO.C_6H_5)$ by the action upon them of benzoyl chloride in the presence of NaOH is utilized for their identification (see pp. 225, 284). Nitrous acid acts upon them as upon the monamines with the formation of glycols:



Among the **diamines** are included several of the products of putrefaction known as **ptomaines**.

Ethylenediamine — $H_2N.(CH_2)_2.NH_2$ — is a strongly alkaline liquid, boiling at 116.5° . With acetyl chloride it forms **diacetyl-ethylene diamine**, $\begin{array}{c} CH_2.NH.CO.CH_3 \\ | \\ CH_2.NH.CO.CH_3 \end{array}$, which is decomposed by heat with formation of a cyclic amidine base, **ethylene-ethenyl amidine**, or



Trimethylenediamine — $H_2N.(CH_2)_3.NH_2$ — is said to have been obtained from the cultures of the comma bacillus. It has been obtained synthetically. It is an alkaline liquid, boiling at 135° .

Tetramethylenediamine—Putrescine — $H_2N.(CH_2)_4.NH_2$ — is produced along with cadaverine, during the putrefaction of muscular tissue, internal organs of man and animals, and of fish, and in the culture media of the comma bacillus from three days to four months. The free base is a colorless liquid (solid below 27°) having a seminal odor, which absorbs CO_2 from the air and unites with acids to form crystalline salts. It is not actively poisonous.

Pentamethylenediamine—Cadaverine — $H_2N.(CH_2)_5.NH_2$ — is iso-

meric with neuridine and is produced during the later stages of putrefaction of many animal tissues, the choline disappearing as this and the other diamines are formed. The free base is a clear syrupy liquid, having a strong disagreeable odor, resembling that of coniine, boils at 175° , and fumes in air. It absorbs CO_2 rapidly, with formation of a crystalline carbonate. Its salts are crystalline. The chloride on dry distillation is decomposed into ammonium chloride and piperidine.

Neuridine— $\text{C}_5\text{H}_{14}\text{N}_2$ —a diamine of undetermined constitution, isomeric with cadaverine, is produced, along with choline, during the earlier stages of putrefaction, particularly of gelatinoid substances, and increases in quantity as putrefaction advances, while the quantity of choline diminishes. The free base is a gelatinous substance, having a very marked seminal odor, readily soluble in water, insoluble in alcohol and in ether. Its chloride is crystalline and very soluble in water. It seems to be non-poisonous when pure.

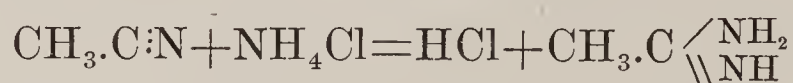
Saprine— $\text{C}_4\text{H}_{16}\text{N}_2$ —another diamine of undetermined constitution has been obtained from putrid spleens and livers after three weeks' putrefaction.

Mydaleine is still another putrid product of undetermined composition, but probably a diamine containing four or five carbon atoms, which forms a difficultly crystallizable, hygroscopic chloride, which is actively poisonous. Five milligrams administered hypodermically to a cat causes death after profuse diarrhea and secretion of saliva, violent convulsions, and paralysis, beginning with the extremities and extending to the muscles of respiration.

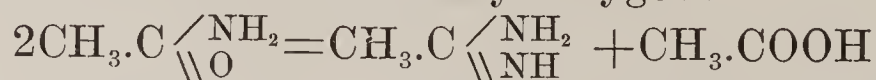
AMIDINES—AMIDOXIMES—HYDROXAMIC ACIDS.

The **amidines** contain both the amido group, NH_2 , and the imido group, NH , and have the general formula: $\text{RC} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{NH} \end{smallmatrix}$, in which R is any univalent hydrocarbon radical.

They are formed by heating the nitriles (p. 305) with ammonium chloride. Thus acetonitrile yields **acetamidine**:



They are also formed by action of HCl upon the amides. Indeed, they may be considered as being derived from the amides (p. 310) by substitution of NH for the carbonyl oxygen:



($\text{CH}_3.\text{C} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{O} \end{smallmatrix}$ = acetamide; $\text{CH}_3.\text{C} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{NH} \end{smallmatrix}$ = acetamidine.) The amidines are monacid bases, very unstable when free.

The **amidoximes** are derived from the amidines by substitution of OH for hydrogen, *e.g.*, $\text{CH}_3.\text{C} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{N.OH} \end{smallmatrix}$, **ethenylamidoxime**. They are

very unstable compounds, formed by the action of hydroxylamine upon nitriles or upon amidines.

Hydroxamic acids contain the **oxime** group, N.OH, while the amido group of the amidine is replaced by hydroxyl: $\text{CH}_3\cdot\text{C}\begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{N.OH} \end{smallmatrix}$ **acetohydroxamic acid**.

GUANIDINE AND ITS DERIVATIVES.

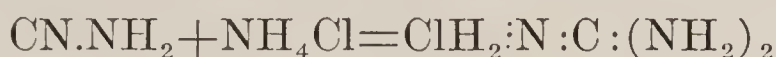
Guanidine—Carbotriamine— CH_5N_3 —was first obtained by oxidation of guanine. It is formed (1) by heating ethyl orthocarbonate with ammonia:



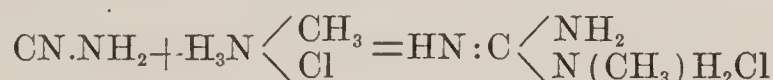
(2) From cyanogen iodide and ammonia:



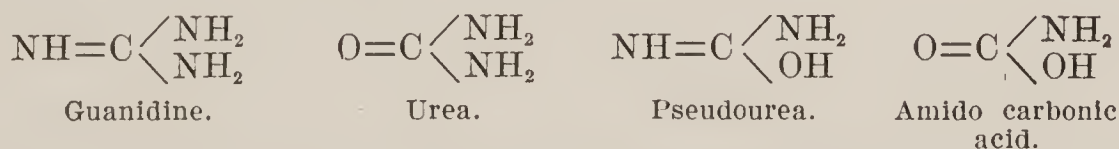
(3) As hydrochloride from cyanamide and ammonium chloride:



Substituted guanidines may be obtained by method (3) by using hydrochlorides of primary amines:



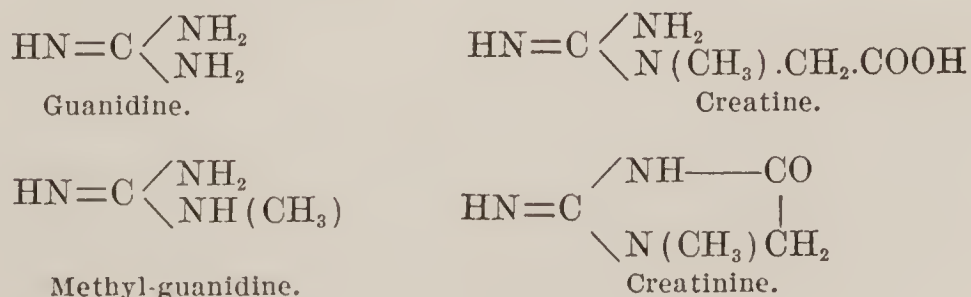
Guanidine, containing the group $\cdot\text{C}\begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{NH} \end{smallmatrix}$, is an amidine. It may also be considered as a triamine, derived from three ammonia molecules, $\text{H}_2\text{N}-\text{C}\begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{NH} \end{smallmatrix}$. It is related to amidocarbonic acid, to urea and to pseudourea, as is indicated by the formulæ:



It is a crystalline solid, which absorbs CO_2 and H_2O from the air, and forms crystalline salts.

Methyl-guanidine — Methyluramine — $\text{HN}:\text{C}(\text{NH}_2)\text{NH}(\text{CH}_3)$ — was first obtained by the oxidation of creatine and of creatinine (see below). It has also been obtained as a product of putrefaction of muscular tissue at a low temperature in closed vessels, when it probably results from the decomposition of creatine. It is a colorless, crystalline, deliquescent, strongly alkaline substance, and is highly poisonous.

The relation of guanidine and methyl-guanidine to each other and to creatine and creatinine is shown by the following formulæ:



Creatine—*Methyl-guanidine acetic acid*— $C_4H_9N_3O_2 + Aq$ —is, as is shown by the above graphic formula, a complex amido-acid. It is a normal constituent of the juices of muscular tissue, brain, blood, and amniotic fluid. It is formed synthetically by the union of methyl glycocoll and cyanamide:



It is best obtained from the flesh of the fowl, which contains 0.32 per cent., or from beef-heart, which contains 0.14 per cent. It is soluble in boiling H_2O and in alcohol, insoluble in ether; crystallizes in brilliant, oblique, rhombic prisms; neutral; tasteless; loses Aq at 100° ; fuses and decomposes at higher temperatures. When long heated with H_2O , or treated with concentrated acids, it loses H_2O , and is converted into creatinine. Baryta water decomposes it into sarcosine and urea. It is not precipitated by silver nitrate, except when it is in excess and in presence of a small quantity of potassium hydroxide. The white precipitate so obtained is soluble in excess of potash, from which a jelly separates, which turns black, slowly at ordinary temperatures, rapidly at 100° . A white precipitate, which turns black when heated, is also formed when a solution of creatine is similarly treated with mercuric chloride and potash.

Creatinine—*Methyl-guanidine acetic lactam*— $C_4H_7N_3O$ —113—a product of the dehydration of creatine, is a normal and constant constituent of the urine and amniotic fluid, and also exists in the blood and muscular tissue.

It crystallizes in oblique, rhombic prisms, soluble in H_2O and in hot alcohol, insoluble in ether. It is a strong base, has an alkaline taste and reaction; expels NH_3 from the ammoniacal salts, and forms well-defined salts, among which is the double chloride of zinc and creatinine $(C_4H_7N_3O)_2ZnCl_2$, obtained in very sparingly soluble, oblique prismatic crystals, when alcoholic solutions of creatinine and zinc chloride are mixed.

HYDRAZINES—HYDRAZIDES.

The **hydrazines** are derivatives of hydrazine or diamidogen, $H_2N.NH_2$ (p. 96), by substitution of aliphatic or aromatic radicals, alcoholic, phenolic or acid, for one or more of the hydrogen atoms in the same way as the amines are derived from ammonia. There are, therefore, primary, secondary, tertiary and quaternary hydrazines; and they may be **symmetrical**, as $C_2H_5HN.NH.C_2H_5$ and $C_6H_5.HN.NH.C_2H_5$, or **unsymmetrical**, as $C_6H_5HN.NH_2$ and $(C_2H_5)_2N.NH_2$. The aliphatic hydrazines are obtained from the alkyl-ureas, by conversion into nitroso-amines, and reduction. Most of the hydrazines, some of which are of considerable interest, are derivatives of phenylhydrazine, $C_6H_5HN.NH_2$, and, containing a cyclic chain C_6H_5 . These

will be considered among the aromatic compounds. The **hydrazides**, corresponding to the amides, contain acidyls.

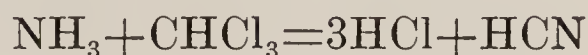
NITRILES—CYANOGEN COMPOUNDS.

These substances may be considered either as compounds of the univalent radical **cyanogen** (CN)', or as paraffins, C_nH_{2n+2} , in which three atoms of hydrogen have been replaced by the trivalent N''' atom, hence **nitriles**, compounds of N with the trivalent radicals C_nH_{2n-1} .

Hydrogen Cyanide—Hydrocyanic acid—Prussic acid—Formo-nitrile—Cyanogen hydride—HC:N—exists ready formed in the juice of *cassava*, and is formed by the action of H_2O upon bitter almonds, cherry-laurel leaves, and other vegetable products containing **amygdalin**, a glucoside, which is decomposed into glucose, benzoic aldehyde (p. 362), and hydrocyanic acid, when warmed with water. It is also formed in a great number of reactions: by the passage of the electric discharge through a mixture of acetylene and nitrogen:



By the action of chloroform on ammonia:



By the distillation of, or the action of HNO_3 upon, many organic substances; by the decomposition of cyanides (see Nitriles, below).

It is always prepared by the decomposition of a cyanide or a ferrocyanide, usually by acting upon potassium ferrocyanide with dilute sulphuric acid, and distilling. Its preparation in the pure form is an operation attended with the most serious danger, and should only be attempted by those well trained in chemical manipulation. For medical uses a very dilute acid is required; the **acidum hydrocyanicum dilutum** (U. S. P.) contains, if freshly and properly prepared, two per cent. of anhydrous acid. That of the French Codex is much stronger—ten per cent.

The pure acid is a colorless, mobile liquid, has a penetrating and characteristic odor; sp. gr. 0.7058 at 7° ; crystallizes at -15° ; boils at 26.5° ; is rapidly decomposed by exposure to light. The dilute acid of the U. S. P. is a colorless liquid, having the odor of the acid; faintly acid, the reddened litmus returning to blue on exposure to air; sp. gr. 0.997; 10 grams of the acid should react without excess with 1.27 gram of silver nitrate. The dilute acid deteriorates on exposure to light, although more slowly than the concentrated; a trace of phosphoric acid added to the solution retards the decomposition.

Most strong acids decompose HCN. The alkalies enter into double decomposition with it to form **cyanides**. It is decomposed by Cl and Br, with formation of cyanogen chloride or bromide. Nascent H converts it into methylvamine.

Analytical Characters.—(1) With silver nitrate: a dense, white ppt.; which is not dissolved on addition of HNO_3 to the liquid, but dissolves when separated and heated with concentrated HNO_3 ; soluble in solutions of alkaline cyanides or thiosulphates. (2) Treated with NH_4HS , evaporated to dryness, and ferric chloride added to the residue: a blood-red color, which is discharged by mercuric chloride. (3) With potash and then a mixture of ferrous and ferric sulphates: a greenish ppt., which is partly dissolved by HCl , leaving a pure dark-blue precipitate. (4) Heated with a dilute solution of picric acid and then cooled: a deep-red color. (5) Moisten a piece of filter-paper with a freshly prepared alcoholic solution of guaiac; dip the paper into a very dilute solution of CuSO_4 , and, after drying, into the liquid to be tested. In the presence of HCN it assumes a deep-blue color. (6) Add a few drops of potassium nitrite solution, then two or three drops of ferric chloride solution, and enough dilute H_2SO_4 to turn the color to yellow. Heat just to boiling; cool, add a few drops of NH_4OH , filter, and add to the filtrate a few drops of dilute, colorless ammonium sulphhydrate: a violet color, changing to blue, then to green and yellow.

Toxicology.—Hydrocyanic acid is a violent poison, whether it is inhaled as vapor, or swallowed, either in the form of dilute acid, of soluble cyanide, or of the pharmaceutical preparations containing it, such as oil of bitter almonds and cherry-laurel water; its action being more rapid when taken by inhalation or in aqueous solution than in other forms. When the medicinal acid is taken in poisonous dose, its lethal effect may seem to be produced instantaneously; nevertheless, several respiratory efforts usually are made after the victim seems to be dead, and instances are not wanting in which there was time for considerable voluntary motion between the time of ingestion of the poison and unconsciousness. In the great majority of cases the patient is either dead or fully under the influence of the poison on the arrival of the physician, who should, however, not neglect to apply the proper remedies if the faintest spark of life remains. Chemical antidotes are, owing to the rapidity of action of the poison, of no avail, although possibly chlorine, recommended as an antidote by many, may have a chemical action on that portion of the acid already absorbed. The treatment indicated is directed to the maintenance of respiration; cold douche, galvanism, artificial respiration, until elimination has removed the poison. If the patient survives an hour after taking the poison, the prognosis becomes very favorable; in the first stages it is exceedingly unfavorable, unless the quantity taken has been very small.

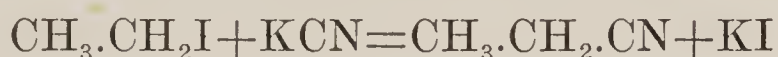
In cases of suspected homicide by hydrocyanic acid, the stomach should never be opened until immediately before the analysis.

Cyanogen Chlorides.—Two polymeric chlorides are known: **Cyanogen chloride**, CNCl , formed by the action of Cl upon anhydrous HCN or upon $\text{Hg}(\text{CN})_2$ in the dark. It is a colorless gas, condensing to a liquid at 15° ; intensely irritating and poisonous. **Tricyanogen chloride**, $\text{C}_3\text{N}_3\text{Cl}_3$, is formed, as a crystalline solid, when anhydrous HCN is acted upon by Cl in sunlight. It fuses at 146° . (See Cyanidine, p. 414.)

Cyanides.—The most important of the simple metallic cyanides are those of K and Ag.

Nitriles.—The hydrocyanic esters of the univalent alcoholic radicals are called **acid nitriles**, because of their formation from the amides, by the reaction given under (3) below. Hydrocyanic acid, being produced from formamide, is **formonitrile**; methyl cyanide, derived from acetamide, is **acetonitrile**, etc. They are also derivable from the ammonium salt of the acid by elimination of the elements of two molecules of water. Their formulæ may be derived from those of the acids by substitution of N for the trivalent OOH of the carboxyl. The acid nitriles are not to be confounded with the acidyl cyanides, which are the nitriles of the ketonic acids.

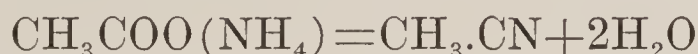
The nitriles are produced: (1) By heating the haloid esters (p. 205) with alcoholic solution of potassium cyanide at 100°:



(2) By distilling a mixture of potassium cyanide and the potassium salt of a monoalkyl sulphate. Thus, ethyl cyanide is produced from potassium ethylsulphate:



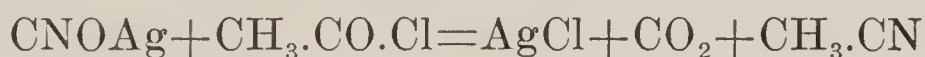
(3) By complete dehydration, by the action of P_2O_5 , of the ammoniacal salt of the acid, or of its amide. Thus acetonitrile is obtained from ammonium acetate:



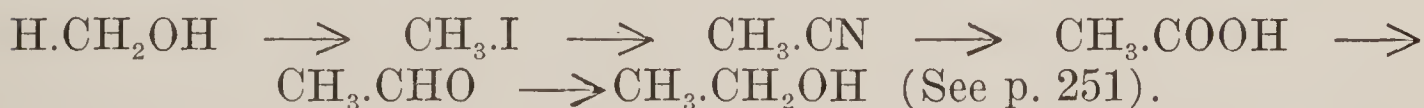
or from acetamide:



(4) By the action of acidyl chlorides upon silver cyanate. Thus, with acetyl chloride, methyl cyanide is formed:



The formation of the nitriles is frequently utilized to pass from a given carbon compound to its next superior homologue. Thus ethyl alcohol may be obtained from methyl alcohol by the steps:



The nitriles combine with nascent hydrogen to form primary amines. Thus acetonitrile forms ethylamine:

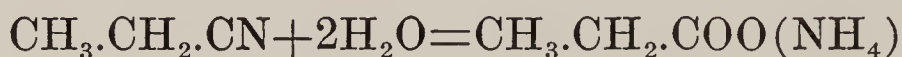


Hydrating agents convert them into the ammonium salts of the corresponding acids. Thus ammonium propionate is derived from ethyl cyanide: $\text{C}_2\text{H}_5.\text{CN} + 2\text{H}_2\text{O} = \text{C}_2\text{H}_5.\text{COO}(\text{NH}_4)$. Or, when acted upon by concentrated sulphuric acid, hydrogen peroxide, or concentrated hydrochloric acid, they take up one molecule of water and form

amides. Thus acetonitrile forms acetamide: $\text{CH}_3.\text{CN} + \text{H}_2\text{O} = \text{CH}_3.\text{CO}.\text{NH}_2$.

Methyl Cyanide—Acetonitrile— $\text{CH}_3.\text{CN}$ —is a colorless liquid, b. p. 81.6° , having an agreeable odor, sparingly soluble in water, obtained by distilling ammonium acetate or acetamide with P_2O_5 .

The **isocyanides**, **carbylamines**, or **carbamines**, are isomeres of the nitriles, which differ from the latter in constitution in that, in the nitriles, the nitrogen is trivalent, and the alkyl group is in union with carbon, *e.g.*, methyl cyanide, $\text{N}\equiv\text{C}-\text{CH}_3$, while in the carbylamines the nitrogen is quinquivalent, and the alkyl is in union with nitrogen, *e.g.*, methyl isocyanide, $\text{C}\equiv\text{N}-\text{CH}_3$. The difference in constitution between the nitriles (alkyl cyanides) and the alkyl isocyanides is shown by the difference in their behavior with hydrating agents. While the cyanides yield the ammonium salts of the corresponding acids:



the isocyanides are split into a primary amine and formic acid:



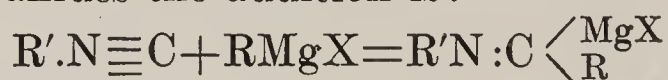
The alkyl magnesium halides act differently upon cyanides and isocyanides. With the former an addition product is formed according to the equation:



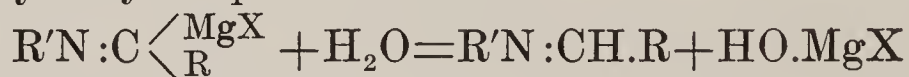
which when hydrolyzed produces ketones:



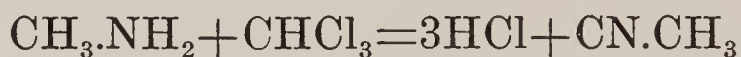
With the isocyanides the addition is:



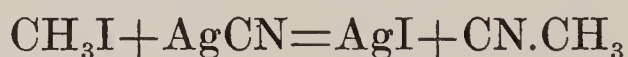
which when hydrolyzed produces imines:



The isocyanides are formed: (1) by the action of a primary mon-amine on chloroform in the presence of caustic potash. Thus methyl isocyanide is derived from methylamine:



(2) By the action of alkyl iodides upon silver cyanide:



Methyl Isocyanide—Methylcarbylamine—Isoacetonitrile— $\text{CH}_3.\text{NC}$ —is a colorless liquid, b. p., 58° , having a disagreeable odor, and giving off highly poisonous vapor. It is formed by the reactions given above, and is said to exist in the venom of toads.

Phenyl Isocyanide—Isobenzonitrile— $\text{C}_6\text{H}_5.\text{NC}$ —is a colorless liquid, not boiling without decomposition, having an intensely disagreeable odor, whose formation is utilized in a test for chloroform.

Both nitriles and isonitriles combine with the hydracids to form

crystalline salts, decomposable by water; the latter much more energetically than the former. They are all volatile liquids; the nitriles having ethereal odors when pure, the isonitriles odors which are very powerful and disagreeable.

Dicyanogen— CN.CN —is prepared by heating mercuric cyanide, and is also formed by passing an electric arc between carbon points in an atmosphere of nitrogen.

It is a colorless gas, has a pronounced odor of bitter almonds: sp. gr., 1.8064 A. It burns in air with a purple flame, giving off N and CO_2 . It is quite soluble in water, but the solutions soon turn brown, and then contain ammonium oxalate and formate, urea, and hydrocyanic acid.

Nitriles of Carbonic and Thiocarbonic Acids.—These constitute the oxygen and sulphur compounds of cyanogen. Thus cyanic acid is the nitrile of carbonic acid: $\text{CO}_3\text{H}(\text{NH}_4) = \text{CONH} + 2\text{H}_2\text{O}$, and thiocyanic acid that of thiocarbonic acid: $\text{CO}_2\text{SH}(\text{NH}_4) = \text{CSNH} + 2\text{H}_2\text{O}$.

Three structural formulæ of these compounds are possible: $\text{N} \equiv \text{C} \cdot \text{OH}$, $\text{O} = \text{C} = \text{N} \cdot \text{H}$, and $\text{C} \equiv \text{N} \cdot \text{OH}$. The first structure is that of the normal cyanic and thiocyanic acids, the second that of the isocyanates and isothiocyanates, the third that of fulminic acid.

Cyanic Acid— NC.OH —is obtained by distillation of cyanuric acid, or, in its salts, by calcining the cyanides in presence of an oxidizing agent, or by the action of dicyanogen upon solutions of the alkalis or alkaline carbonates.

It is a colorless liquid, only stable below 0° ; has a strong odor, resembling that of formic acid; and is soluble in water; gives off an irritating vapor; is vesicating to the skin; and is changed by exposure to air into its polymere, **cyamelide**, a white, porcelain-like solid.

Cyanuric Acid — *Tricyanic acid* — *Trioxycyanidine* — $\text{HO} \cdot \text{C} \begin{array}{c} // \text{N} - \text{C}(\text{OH}) \\ \backslash \text{N} = \text{C}(\text{OH}) \end{array} \backslash \text{N}$ —is produced by dry distillation of uric acid; by the action of heat or of Cl upon urea; by heating tricyanogen chloride or bromide with water or with alkalis. It forms colorless crystals, odorless, almost tasteless, feebly acid, rather soluble in water. It is tribasic. It may be dissolved in strong H_2SO_4 or HNO_3 without decomposition, but, when boiled with acids or alkalis, it is decomposed into carbon dioxide and ammonia; and, when distilled, into cyanic acid.

The ordinary potassium and ammonium cyanates are regarded as **isocyanates**, salts of **isocyanic acid**, or **carbimide**, $\text{O} : \text{C} : \text{NH}$. The ammonium salt, $\text{O} : \text{C} : \text{N}(\text{NH}_4)$, is converted into its isomere, urea, $\text{H}_2\text{N.CO.NH}_2$, by evaporation of its solution. The isocyanic esters serve for the generation of the alkyl ureas.

Fulminic Acid—*Carbyloxime*— $\text{C} \equiv \text{N.OH}$ —is a strongly acid substance, having the odor and poisonous qualities of hydrocyanic acid,

whose Ag and Hg salts are formed by the action of nitrous acid upon alcohol and silver, or mercuric, nitrate. **Mercuric fulminate**, or **fulminating mercury**, crystallizes in white, soluble needles, and explodes violently upon shock. It is used in percussion caps, primers and cartridges. **Silver fulminate** is more violently explosive than the mercurial salt. **Fulminating gold** is not a fulminate, but **auro-amidoimide**, $\text{Au}(\text{NH})\text{NH}_2 + 3\text{H}_2\text{O}$.

Fulminuric Acid— $\text{CN}.\text{CH}(\text{NO}_2).\text{C} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{NH} \end{smallmatrix}$ —metamerie with cyanuric, and polymeric with cyanic and isocyanic acids, is a derivative of tartronic acid, $\text{COOH}.\text{CHOH}.\text{COOH}$; whose alkali salts are formed by boiling solutions of alkaline chlorides with mercuric fulminate.

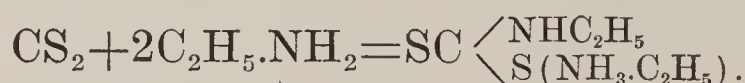
Thiocyanic Acid—*Sulphocyanic acid*—*Cyanogen sulphhydrate*— $\text{N} \equiv \text{C}.\text{SH}$ —is obtained by decomposition of its salts, which are formed by boiling solutions of the cyanides with sulphur; by the action of dicyanogen upon the metallic sulphides; and in several other ways.

The free acid is a colorless liquid, crystallizes at -12.5° , acid in reaction. The prominent reaction of the acid and of its salts is the formation of a deep-red color with the ferric salts; the color being discharged by mercuric chloride solution.

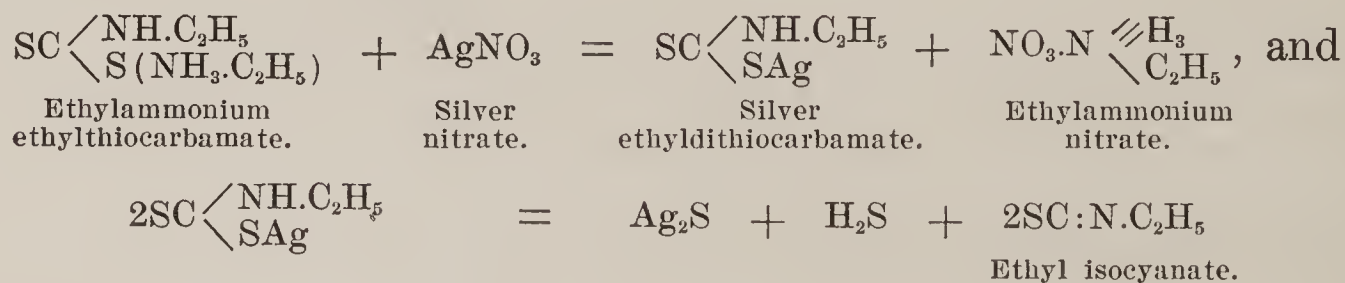
Thiocyanates exist in the human saliva and in the stomach-contents, in small amount. The free acid is poisonous.

Isothiocyanic Esters—*Mustard oils*—Isothiocyanic acid, $\text{S}:\text{C}:\text{NH}$, is not known in the free state. Its esters are called mustard oils, from the most important of the class, allyl isothiocyanate, which is the essential oil of mustard.

The mustard oils are obtained: (1) by mixing ether solutions of primary amines and carbon disulphide, and evaporating the solutions, the amine salts of alkyl dithiocarbamic acids are formed:



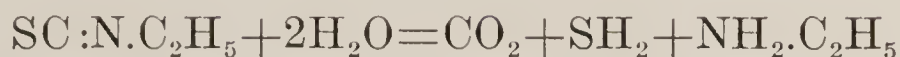
On boiling aqueous solutions of these with AgNO_3 , FeCl_3 or HgCl_2 , the metallic sulphides are precipitated, and hydrogen sulphide and the mustard oils are formed, the latter distilling over. The reaction takes place in two stages:



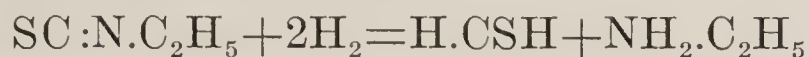
Hoffman's test for the primary amines (p. 295) is based upon these reactions.

The mustard oils are liquids, insoluble in water, giving off vapors of penetrating odor and irritating to the eyes. When heated with

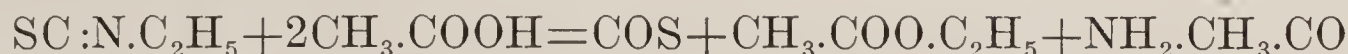
water under pressure to 200° , or with hydrochloric acid to 100° , they are decomposed into carbon dioxide, hydrogen sulphide and amines:



Heating with dilute H_2SO_4 decomposes them into amines and carbon oxysulphide, COS . With nascent hydrogen they yield thioformaldehyde and a primary amine:

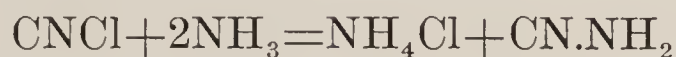


Heated with monocarboxylic acids they form carbon oxysulphide, esters, and monamides:

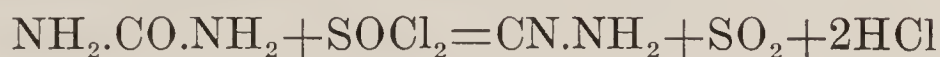


Their alcoholic solutions, when boiled with HgO , yield isocyanic esters, which are converted by water into the corresponding compound ureas.

Cyanamide— CN.NH_2 —is the nitrile of carbamic acid: $\text{OC:NH}_2.\text{O.NH}_4.-2\text{H}_2\text{O}=\text{CN.NH}_2$. It is formed by the action of cyanogen chloride upon ammonia:



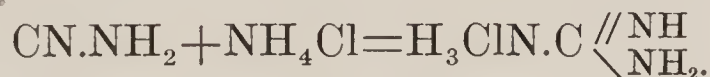
or by the action of thionyl chloride upon urea:



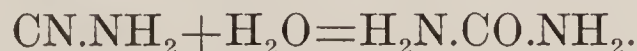
It forms colorless crystals, soluble in water, alcohol or ether. Corresponding to it are substituted cyanamides, which may be formed by using a primary amine in place of ammonia in the above-mentioned method of preparation:



Heated with ammonium chloride it forms guanidine hydrochloride:



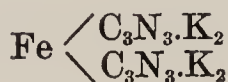
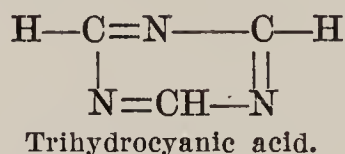
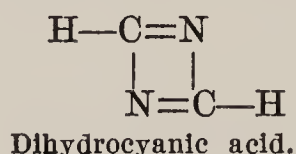
Hydrating agents convert it into urea:



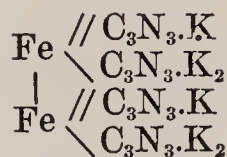
Metallocyanides.—The metallic compounds of cyanogen, the cyanides, may be divided into three classes: (1) the simple cyanides, such as potassium, silver, or mercuric cyanide, which resemble in constitution and general characters the chlorides, bromides, and iodides; (2) the double cyanides, such as $\text{AgK}(\text{CN})_2$, or $\text{HgK}_2(\text{CN})_4$, which are constituted like other double salts. These salts have crystalline forms and solubilities of their own, independent of those of the simple cyanide of which they are made up. They are readily decomposed by cold acids, with liberation of hydrocyanic acid; (3) compound cyanides, or metallocyanides, in which the cyanogen groups are more intimately attached to the metal, in such manner that the ordinary analytical characters of the metals are completely masked; and when

they are decomposed by cold acids hydrocyanic acid is not liberated, but a complex metallohydrocyanic acid, corresponding in constitution to the salt. The metals entering into the composition of the metalocyanides are iron (ferro- and ferricyanides), cobalt (cobalticyanides), and platinum (platinocyanides); also chromium and manganese in the *ic* form.

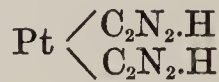
The metalocyanides are considered as derivatives of two hypothetical acids, polymeres of hydrocyanic acid: **dihydrocyanic acid** and **trihydrocyanic acid**, which, in the hydrometallocyanic acids and their salts, are combined with the constituent metal, with loss of hydrogen, as shown in the following formulæ:



Potassium
ferrocyanide.



Potassium
ferricyanide



Hydroplatinocyanic
acid.

Hydronitroprussic Acid— $\text{Fe}(\text{CN})_5(\text{NO})\text{H}_2$ —contains the *nitroso* group NO, and is produced when potassium ferrocyanide is acted upon by nitric acid. Its sodium salt, **sodium nitroprusside**, is formed by neutralizing the acid with sodium carbonate. It forms brilliant red prisms; and is used as a test for sulphides, with which it forms a violet color. (See test No. 6, Hydrocyanic acid, p. 304.)

AMIDES.

These compounds are similar in constitution to the amines (p. 292), from which they differ in that the radicals substituted in ammonia are acidyls in place of alkyls: $\text{N} \begin{array}{l} \diagup \text{CO}.\text{CH}_3 \\ \diagdown \text{H}_2 \end{array}$; $\text{N} \begin{array}{l} \diagup (\text{CO}.\text{CH}_3)_2 \\ \diagdown \text{H} \end{array}$; $\text{N}(\text{CO}.\text{CH}_3)_3$.

Like the amines they are classified into **monamides**, **diamides** and **triamides**, according as they are derived from one, two, or three molecules of ammonia.

Mixed amides are also known, produced by the substitution of acid radicals for the remaining hydrogen of the primary and secondary amines, *e.g.*, diethyl acetamide: $\text{CH}_3\text{CO}(\text{C}_2\text{H}_5)_2\text{N}$.

MONAMIDES—AMIC ACIDS.

Like the monamines, the monamides are **primary**, **secondary**, or **tertiary**, as they contain one, two or three substituted radicals.

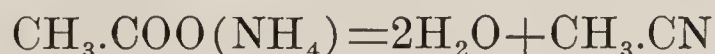
The primary monamides corresponding to the monocarboxylic acids may also be considered as being derived from those acids by

substitution of NH_2 for the OH of the group COOH ; as the amines are derivable from the alcohols by substitution of NH_2 for OH in CH_2OH , CHOH or COH . Thus acetamide, $\text{CH}_3\text{CO.NH}_2$ is derived from acetic acid, $\text{CH}_3\text{CO.OH}$.

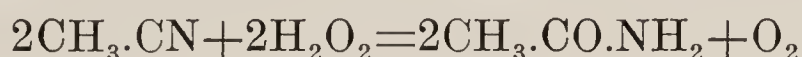
The **primary monamides** are formed: (1) by the action of heat upon the ammonium salt of the acid, with elimination of the elements of one molecule of water:



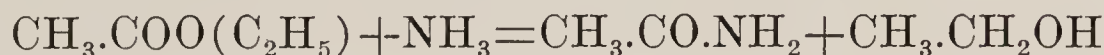
It will be remembered that the nitriles (p. 305) are derived from the ammoniacal salts by elimination of two molecules of water:



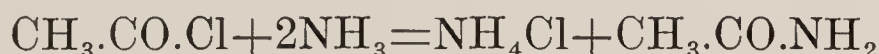
(2) By addition of H_2O to the nitriles. Thus hydrogen peroxide in alkaline solution converts acetonitrile into acetamide:



(3) By the action of ammonia upon esters. Thus, ethyl acetate and ammonia produce acetamide and ethylic alcohol:



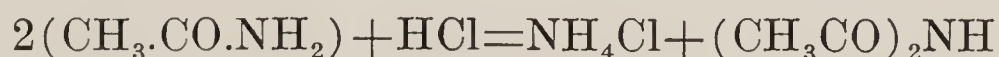
(4) By the action of an acidyl chloride upon dry ammonia. Thus, acetamide is produced by acetyl chloride:



The **secondary monamides** are obtained: (1) by the action of acidyl chlorides upon the primary monamides. Thus, diacetamide is produced from monacetamide:



(2) By the action of hydrochloric acid upon the primary monamides at high temperatures:



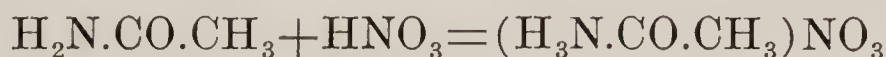
The tertiary amides of this series have been imperfectly studied. Some have been obtained by the action of acidyl chlorides upon metallic derivatives of secondary amides:



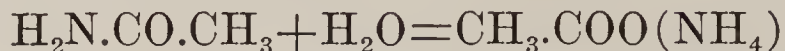
or by the union of anhydrides and nitriles at 200° :



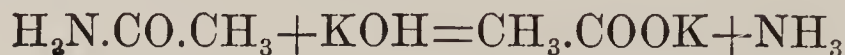
The **primary monamides** of the fatty acids are solid, crystallizable, neutral in reaction, volatile without decomposition, mostly soluble in alcohol and ether, and mostly capable of uniting with acids to form compounds similar in constitution to the ammoniacal salts:



They are capable of uniting with H_2O to form the ammoniacal salts of the corresponding acids:

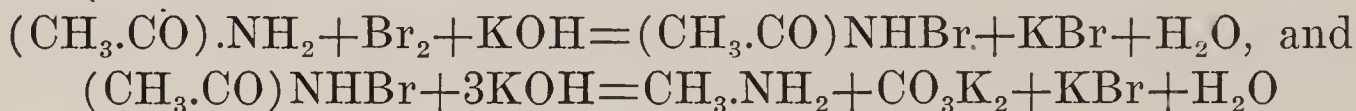


And with the alkaline hydroxides to form the metallic salts of the corresponding acids and ammonia:



They are converted into amines containing one atom of carbon less than themselves by the action of bromine and alkali. The **secondary monamides**, containing two radicals of the fatty series, are acid in reaction, and their remaining atom of extra-radical hydrogen may be replaced by an electro-positive atom.

The action of bromine on the amides in alkaline solution, results in the formation of amines containing one atom of carbon less. The reaction takes place in two stages, with intermediate formation of a **bromamide**:



As the amides are readily obtained by dehydration of the NH_4 salts of the acids, and as the amines yield alcohols which may in turn be oxidized to acids:



this offers a means of "stepping down."

Formamide— CHO.NH_2 —45—is a colorless liquid, soluble in H_2O and in alcohol, boils at 192° – 195° , suffering partial decomposition, obtained by heating ethyl formate with an alcoholic solution of ammonia, or by the dry distillation of ammonium formate. It is decomposed by dehydrating agents, with formation of hydrocyanic acid: $\text{H}_2\text{N}(\text{H.CO}) = \text{HCN} + \text{H}_2\text{O}$. **Mercury formamide** is obtained in solution by gently heating freshly-precipitated mercuric oxide with H_2O and formamide.

Under the name **chloralamide** a compound, formed by the union of chloral and formamide, and having the constitution, $\text{CCl}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH}.\text{CHO} \end{smallmatrix}$ has been used as a hypnotic. It forms colorless, odorless, faintly bitter crystals, fusible at 115° , sparingly soluble in water. It is decomposed by alkalies, chloroform and ammonia being among the products of the decomposition. It is not affected by acids.

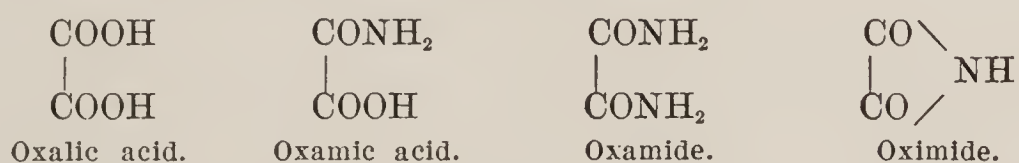
Chloralimide— $\text{CCl}_3.\text{C} \begin{smallmatrix} \text{NH} \\ // \\ \text{H} \end{smallmatrix}$ —is another related derivative, formed by the action of ammonium acetate upon chloral hydrate, or by heating chloral ammonia. It is a crystalline solid, sparingly soluble in water, readily soluble in ether and in alcohol. When heated to 180° it is decomposed into chloroform and formamide.

Acetamide— $\text{CH}_3.\text{CO.NH}_2$ —is obtained by heating, under pres-

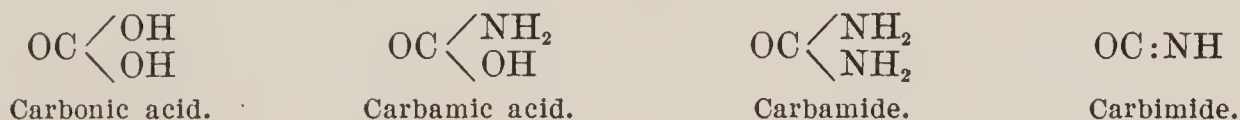
sure, a mixture of ethyl acetate and ammonium hydroxide, and purifying by distillation. It is solid, crystalline, very soluble in H_2O , alcohol, and ether; fuses at 82° ; boils at 222° ; has a sweetish, cooling taste, and an odor of mice. Boiling potassium hydroxide solution decomposes it into potassium acetate and ammonia. Phosphoric anhydride deprives it of H_2O , and forms with it **acetonitrile** or **methyl cyanide**: $\text{H}_2\text{N}.\text{CO}.\text{CH}_3=\text{CH}_3.\text{CN}+\text{H}_2\text{O}$.

AMIDES OF DICARBOXYLIC ACIDS.

As the hydramines, the diamines (p. 296) and the imines are all derivable from the dihydric alcohols, by substitution of NH_2 for OH in the first, of 2NH_2 for 2OH in the second, and of NH for 2OH in the last, so amic acids, diamides, and imides are correspondingly derived from the dicarboxylic acids:



and, recognizing that carbonic acid is a pure dicarboxylic acid, although not a member of the oxalic series, we have:



Amic acids are, therefore, acids derived from two carboxylic acid groups by substituting NH_2 for one OH .

Carbamic Acid—*Amidoformic Acid*— $\text{H}_2\text{N}.\text{CO}.\text{OH}$ —is not known in the free state, being decomposed into CO_2 and NH_3 , but ammonium carbamate is formed whenever ammonia and carbon dioxide are in contact: $\text{CO}_2+2\text{NH}_3=\text{H}_2\text{N}.\text{CO}.\text{O}(\text{NH}_4)$, and it therefore exists in commercial ammonium carbonate, and is formed by oxidation of many carbon-nitrogen compounds, notably amido-acids, in alkaline solution. It exists normally in the blood and urine, and is formed in the system as an intermediate product between amido-acids and urea. It is obtained by directing dry ammonia and carbon dioxide into cold absolute alcohol, as a white crystalline precipitate.

The esters of carbamic acid, called **urethanes**, are more stable than its salts. They are formed by the action of ammonia upon the carbonic esters:



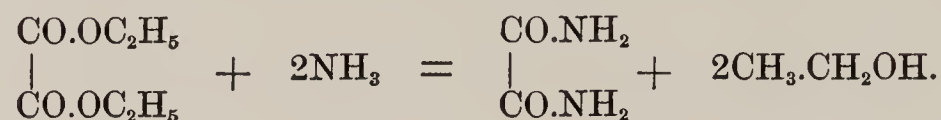
and by the action of cyanogen chloride upon alcohols:



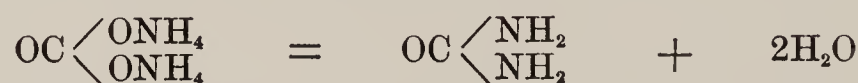
Ethyl urethane, produced by the above reactions, forms thin, large, transparent plates, f. p. 50° , b. p. 184° , very soluble in water

and in alcohol. It is used as a hypnotic, either alone or combined with chloral in **uralium**, or **somnal**. **Phenyl urethane**, $\text{H}_2\text{N.CO.O}(\text{C}_6\text{H}_5)$, is a light, white powder, almost insoluble in water, very soluble in alcohol, which is used as an antipyretic under the name **euphorine**.

The **primary diamides** only are acyclic compounds (see diamines, p. 298). They are formed: (1) by the action of ammonia upon the neutral esters. Thus ethyl oxalate yields oxamide:

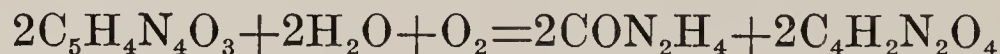


(2) By heating the neutral ammonium salt of the corresponding acid. Thus ammonium carbonate yields carbamide:

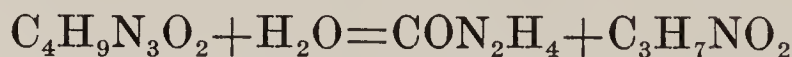


Carbamide—Urea— $\text{H}_2\text{N.CO.NH}_2$ —exists in the urine of mammalia, and, in smaller quantity, in the excrement of birds, fishes and some reptiles; also in the mammalian blood, chyle, lymph, liver, spleen, lungs, brain, vitreous and aqueous humors, saliva, perspiration, bile, milk, amniotic and allantoic fluids, and in serous fluids.

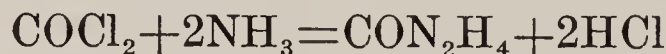
Urea is formed by the methods given above; also, (1) as a product of decomposition of uric acid, usually by oxidation. Thus nitric acid oxidizes uric acid to urea and alloxan:



(2) By the hydrolysis of creatine. Thus urea and sarcosine are formed by the action of KOH upon creatine:



(3) By the action of carbonyl chloride upon dry ammonia:

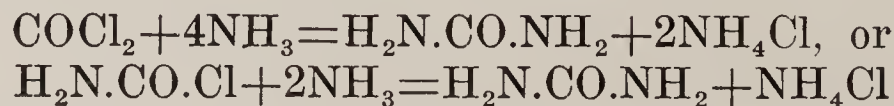


(4) By the action of barium hydroxide upon guanidine (p. 301), or upon the hexon bases, lysine and arginine, products of decomposition of the proteins.

(5) By atomic transposition of its isomere, ammonium isocyanate, by heat:



(6) By the action of ammonia upon phosgene or upon urea chlorides:



(7) By heating ammonium carbamate to 130° :



(8) By the action of ammonia upon urethane:



Urea crystallizes in long rhombic needles or prisms. It is colorless and odorless, and has a cooling taste, somewhat resembling that of saltpeter. It is neutral in reaction, although basic in character; soluble in one part of water, in five parts of cold alcohol, and in one part of boiling alcohol, sparingly soluble in amylic alcohol and in acetic ether, and still less soluble in ether. It fuses at 132° .

When heated a few degrees above its fusing point urea appears to boil, giving off ammonia and ammonium carbonate, and finally leaves a dry, solid residue, consisting of **ammelide**, $\text{C}_3\text{H}_4\text{N}_4\text{O}_2$, **cyanuric acid**, $\text{C}_3\text{O}_3\text{N}_3\text{H}_3$, and **biuret**, $\text{C}_2\text{O}_2\text{N}_3\text{H}_5$. This residue, dissolved in water, gives a fine red-violet color with KOH and CuSO_4 (Biuret reaction). When added to a concentrated solution of furfureole and hydrochloric acid, solid urea or urea nitrate forms a yellow solution, changing in color to green, blue and intense purple-violet. After a time the mixture thickens and blackens (Schiff's reaction).

Dilute aqueous solutions of urea are not decomposed by boiling; but if the solution is concentrated, or the boiling prolonged, or the temperature raised above 100° , the urea is partly decomposed into CO_2 and NH_3 . The same decomposition takes place more rapidly and completely under pressure at 140° . It is also caused by bacterial action and by a urinary enzyme.

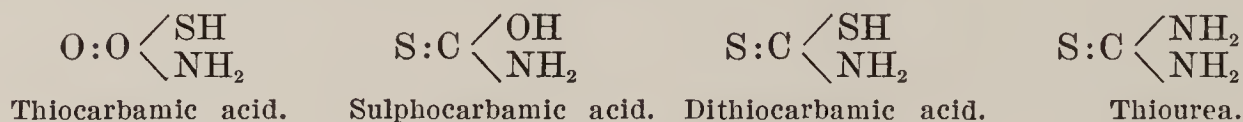
Urea is decomposed into carbon dioxide, water and nitrogen by the alkaline hypochlorites and hypobromites, by chlorine and by nitrous acid. Strong acids and alkalies decompose it into carbon dioxide and ammonia.

Urea forms definite compounds, not only with acids, but also with certain salts and oxides. **Urea nitrate**— $\text{H}_2\text{N.CO.NH}_3.\text{NO}_3$ —forms, in white crystals, when a concentrated solution of urea is treated with nitric acid in the cold. It is much less soluble than urea, especially in presence of an excess of nitric acid. It is decomposed by evaporation of its solutions. **Urea oxalate**— $\text{CO}:(\text{NH}_3)_2:\text{O}_4\text{C}_2$ —separates as a fine, crystalline powder, from mixed concentrated aqueous solutions of urea and oxalic acid. Its solutions may be evaporated without decomposition.

When solutions containing molecular weights of urea and sodium chloride are evaporated, prismatic crystals, containing CON_2H_4 , $\text{NaCl} + \text{H}_2\text{O}$ are obtained. Urea forms several compounds with mercuric oxide. Of these, the compound $(\text{CON}_2\text{H}_4)_2, 4\text{HgO}$, containing 72 parts of HgO for 10 parts of urea, is formed as a white, amorphous precipitate when a dilute solution of mercuric nitrate is gradually added to a dilute, alkaline solution of urea, and the excess of acid neutralized from time to time.

THIOUREA AND THIOCARBAMIC ACIDS.

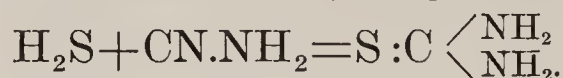
The thio-compounds, corresponding to carbamic acid and to urea, in which oxygen is replaced by sulphur, exist either in their own forms or in their derivatives. Thus:



Thiocarbamic acid and **sulphocarbamic acid** are known only in their esters. **Dithiocarbamic acid** may be obtained by decomposition of its ammonium salt, which is produced by the action of ammonia in alcoholic solution upon carbon disulphide: $\text{CS}_2 + 2\text{NH}_3 = \text{S}:\text{C} \begin{array}{l} \diagup \text{S}(\text{NH}_4) \\ \diagdown \text{NH}_2 \end{array}$

Similarly, the amine salts of the alkyl-dithiocarbamic acids are formed by the action of the primary amines upon carbon disulphide.

Thiourea is obtained by heating ammonium isothiocyanate: $\text{S}:\text{C}:\text{N}(\text{NH}_4) = \text{S}:\text{C} \begin{array}{l} \diagup \text{NH}_2 \\ \diagdown \text{NH}_2 \end{array}$, as urea is obtained from the isocyanate. It is also formed by the action of hydrogen sulphide upon cyanamide:



It is decomposed by boiling acids or alkalies into CO_2 , NH_3 , and H_2S . It forms salts, and alkyl, phenyl and acidyl derivatives similar to those of urea. By addition with alkyl halides thiourea forms salts of alkyl thiopseudoureas, corresponding to pseudourea, which are used in certain cyclic syntheses:



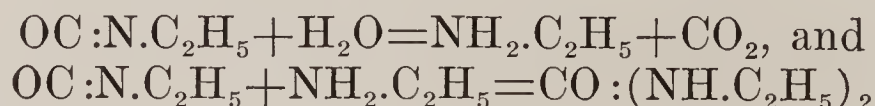
COMPOUND UREAS.

These compounds, which are exceedingly numerous, may be considered as derived from urea by the substitution of one or more alcoholic or acid radicals for hydrogen atoms.

Those containing alcoholic radicals, **alkyl ureas**, such as ethyl urea, $\text{CO} \begin{array}{l} \diagup \text{NH}_2 \\ \diagdown \text{NH.C}_2\text{H}_5 \end{array}$, are obtained: (1) By the action of primary or secondary amines upon isocyanic esters:



(2) By heating the isocyanic esters with water, the amines and carbonic acid being formed as intermediate products:



(3) By condensation of amines with urea chloride.

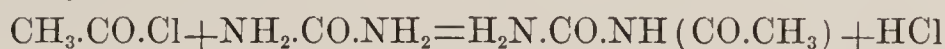
Those containing acid radicals have received the distinctive name of **ureides**. Of these, some are **monureides**, derived from a single

molecule of urea, others **diureides**, derived from two molecules. Some of the monureides are open chain compounds, but the most important of them, and all the diureides except carbonyl diurea are cyclic compounds, derivatives of glyoxalin, pyrimidin or cyanidin. Thus

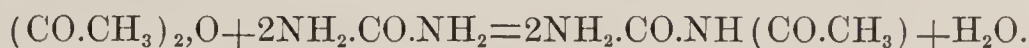
there are two ureides, corresponding to glycollic acid, $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COOH} \end{array}$: one, **hydantoic acid**, an open chain ureide: $\text{CO} \begin{array}{l} \swarrow \text{NH}_2 \\ \searrow \text{NH} \cdot \text{CH}_2 \cdot \text{COOH} \end{array}$; the other, **hydantoin**, a cyclic compound: $\text{CO} \begin{array}{l} \swarrow \text{NH} \cdot \text{CH}_2 \\ \searrow \text{NH} \cdot \text{CO} \end{array}$

Only the acyclic ureides will be here considered, the cyclic ones will be referred to as derivatives of their parent substances.

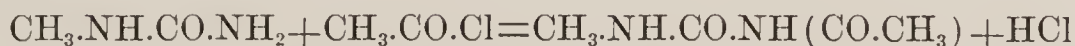
The **monacidyl monureides**, containing a single acidyl, are formed by the action of acidyl chlorides or anhydrides upon urea. Thus acetyl-urea is obtained with acetyl chloride:



or with acetic anhydride:



Mixed ureides, containing an alkyl and an acidyl, are formed in like manner from alkyl-ureas. Thus methyl-urea and acetyl chloride form methyl-acetyl-urea:



Such mixed ureides are also formed by the action of bromine and potassium hydroxide upon the amides, by reactions comparable with those which produce the monamines (p. 294). Thus methyl-acetyl-urea is formed from acetamide:

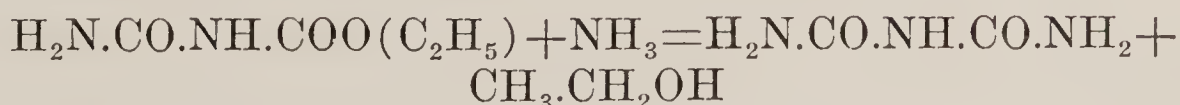


The **diacidyl-ureides** are formed by the action of phosgene (carbonyl chloride) upon the amides. Thus acetamide yields diacetyl-urea:

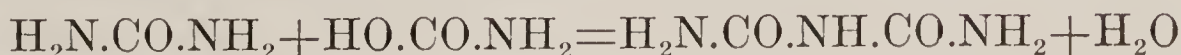


Allophanic acid— $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{COOH}$ —the simplest of the acyclic monureides, is that of carbonic acid, $\text{HO} \cdot \text{CO} \cdot \text{OH}$, and is known only in its esters.

Biuret— $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ —is both the amide of allophanic acid, and the monureide of carbamic acid, $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{OH}$. It is formed by heating the allophanic esters with ammonia:



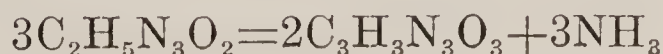
By condensation of urea and carbamic acid:



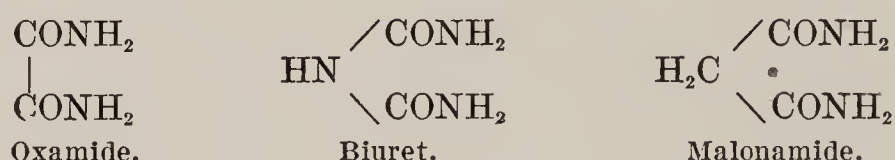
And by heating urea to about 150° :



When further heated it is itself decomposed to cyanuric acid and ammonia:

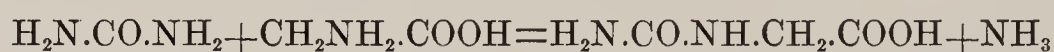


It forms crystals, soluble in water, f. p. 190° . It is chiefly of interest in connection with the **biuret reaction**, which consists in the formation of a red-violet liquid when biuret is heated with a dilute solution of CuSO_4 alkalized with KOH (see Fehling's test). The reaction is due to the formation of a compound, $\text{Cu}[\text{NH}_2(\text{OH}).\text{CO}.\text{NH}.\text{CO}.\text{NH}_2(\text{OH})\text{K}]_2$, which has been obtained in red crystals. Or NiSO_4 may be used in place of CuSO_4 , in which case an orange colored liquid is produced. The biuret reaction is given by many substances other than biuret, such as malonamide, oxamide, aspartic diamide, albumins, albumoses, peptones, etc., and is considered to be proof of the presence in the substance giving it of two amido-carbonyl groups, CONH_2 , attached to each other, or to N or C, as in:



The reaction is also given by glycolamide and sarcosine amide, which contain the grouping: $\text{H}_2\text{N}.\text{CH}_2.\text{CO}.\text{NH}_2$.

Hydantoic Acid—Glycoluric Acid— $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CH}_2.\text{COOH}$ —the next superior homologue of allophanic acid, is the acyclic monureide of glycollic acid, $\text{CH}_2\text{OH}.\text{COOH}$, and is obtained as its Ba salt by hydration of the corresponding cyclic monureide, hydantoin, by BaH_2O_2 . (p. 395). It is also formed by condensation of urea and amido acetic acid at 120° :



Oxaluric Acid— $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CO}.\text{COOH}$ —is the acyclic monureide of oxalic acid, and is obtained in its salts by hydration of those of the cyclic monureide, oxalylurea. The free acid is a white, crystalline powder, sparingly soluble in water. It is easily further hydrolyzed to urea and oxalic acid by heating with alkalis, or even with water. Its ammonium salts exist in the urine in small amount.

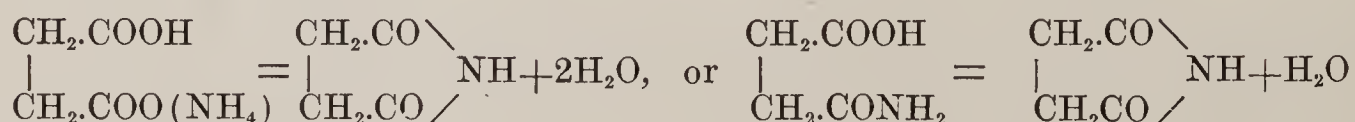
Carbonyl Diurea— $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CO}.\text{HN}.\text{CO}.\text{NH}_2$ —the only acyclic diureide, is formed by the union of two urea molecules, with loss of H_2 , by the carbonyl group, brought about by the action of carbonyl chloride upon urea:



It is a sparingly soluble, crystalline powder, which is split by heat into cyanuric acid and ammonia:



Imides are compounds derivable either by substitution of an acidylene for H_2 in a single NH_3 molecule, or by substitution of the imide group, NH , for $(\text{OH})_2$ in the carboxyls of a dicarboxylic acid. They are obtained by the complete dehydration of the ammonium salts of the acids, or similarly from the amic acids (see pp. 312, 313). Thus monoammonic succinate, or succinamic acid yields succinimide:



The imides, therefore, except **carbimide**, corresponding to carbonic acid, which is isocyanic acid, $\text{O}:\text{C}:\text{N}.\text{H}$ (p. 307), are heterocyclic compounds. The imides,

when acted upon by alkalies or baryta water, produce the salts of the amic acids. Thus succinimide and caustic potash form potassium succinamate.

NITROGEN DERIVATIVES OF ALCOHOLS, ALDEHYDES AND KETONES.

Nitro derivatives of the alcohols, aldehydes, and ketones in which the NO_2 is substituted for OH or for O, such as $\text{CH}_3\text{CH}_2(\text{NO}_2)$ and $\text{CH}_3\text{CH}(\text{NO}_2)_2$ and $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_3$ are mono- or dinitro-paraffins. Besides these, **nitro alcohols** are also known, in which the NO_2 is substituted in a hydrocarbon group, *e.g.*, **nitro-ethyl alcohol**, $\text{CH}_2(\text{NO}_2)\text{CH}_2\text{OH}$.

Amido-alcohols, such as **amido-ethyl alcohol**, or **oxethylamine**, $\text{CH}_2(\text{NH}_2)\text{CH}_2\text{OH}$, may also be considered as derived from the glycols by substitution of NH_2 for OH. These are the **oxyamines**, **hydroxamines**, **hydramines**, or **oxyamine bases**, among which are choline and neurine.

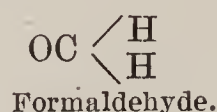
Aldehyde-ammonia—*Ethidene hydroxamine* — $\text{CH}_3\text{CH} \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$ — isomeric with ethylene hydroxamine, $\text{CH}_2(\text{NH}_2)\text{CH}_2\text{OH}$, may be considered as an amido-ethyl alcohol in which the NH_2 is substituted for H in the methoxyl group, $\text{CH}_3\text{CH}(\text{NH}_2)\text{OH}$. It is obtained by the action of dry NH_3 upon an ethereal solution of acetic aldehyde: $\text{CH}_3\text{CHO} + \text{NH}_3 = \text{CH}_3\text{CH}(\text{NH}_2)\text{OH}$. It is a crystalline solid, sparingly soluble in water, alkaline, f. p. 80° .

The corresponding compound derivable from formic aldehyde: $\text{HCH}(\text{NH}_2)\text{OH}$, is not known; but when formaldehyde and ammonia react **hexamethylene tetramine**, $(\text{CH}_2)_6\text{N}_4$, is produced: $6\text{HCHO} + 4\text{NH}_3 = (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O}$. This is a crystalline solid, very soluble in water, which decomposes when heated, and behaves as a monacid base. It is decomposed by weak acids and by acid salts, in the reverse manner to its formation, with liberation of formic aldehyde, a reaction which is probably caused by the acid sodium phosphate of the urine, and explains its action as a urinary antiseptic, for which purpose it is used under the names *formin* and *urotropin*.

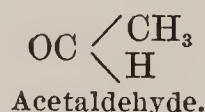
Amido aldehydes, such as **amido acetaldehyde**, $\text{CH}_2(\text{NH}_2)\text{CHO}$, are also known.

Acetonamines—The action of ammonia upon acetone causes a condensation of two or three molecules of acetone with one of ammonia, with formation of **diacetoneamine**: $\text{CH}_3\text{COCH} \begin{smallmatrix} \text{CH}_3 \\ (\text{CH}_3)_2 \end{smallmatrix} \text{C.NH}_2$, a colorless liquid; and **triacetoneamine**: $\text{OC} \begin{smallmatrix} \text{CH}_2\text{C}(\text{CH}_3)_2 \\ \text{CH}_2\text{C}(\text{CH}_3)_2 \end{smallmatrix} \text{NH}$, a crystalline solid, f. p. 40° . Triacetoneamine and its relative vinyl diacetoneamine are derivatives of piperidine, and are the nuclei of the artificial local anesthetics α and β eucaine. Alkyl derivatives of these are formed when amines are used in place of ammonia. **Amido acetones**, or **amido ketones**, such as $\text{CH}_3\text{COCH}_2(\text{NH}_2)$, **amido acetone**, are also known.

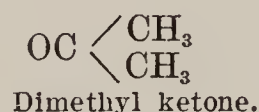
Aldoximes, and **ketoximes** or **acetoximes** are isomeric compounds derivable from the aldehydes and ketones by substitution of the **oxime** group, $=N.OH$, for oxygen. As the aldehydes and ketones are derivatives of formic aldehyde by substitution of alkyls for H, so the aldoximes and ketoximes are referable to **carboxime**, the oxime of formic aldehyde:



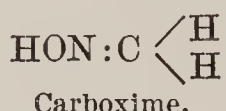
Formaldehyde.



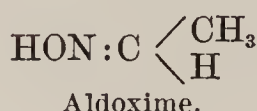
Acetaldehyde.



Dimethyl ketone.



Carboxime.

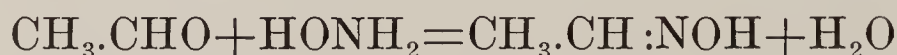


Aldoxime.

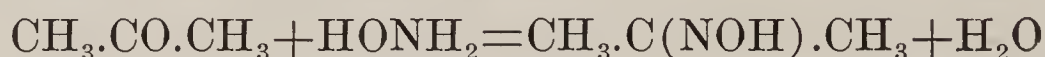


Ketoxime.

They are formed by the action of hydroxylamine upon aldehydes or ketones in alkaline solution, the aldoximes more readily than the ketoximes. Thus **acetaldoxime** is obtained from acetic aldehyde:

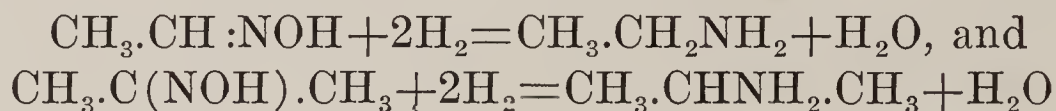


and **acetoxime** from dimethyl ketone:

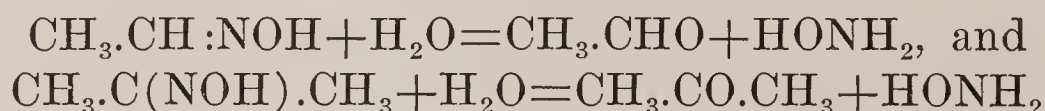


The aldoximes are colorless liquids, miscible with water; the ketoximes crystalline solids, soluble in water.

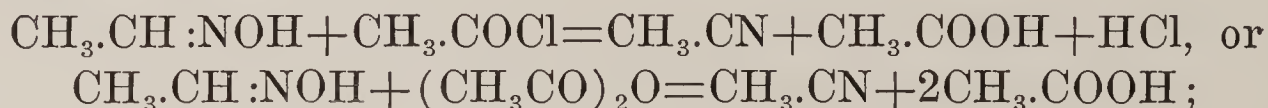
Nascent hydrogen reduces both aldoximes and ketoximes to amines, those from the aldoximes being amines of primary alcohols and those from the ketoximes, amines of secondary alcohols:



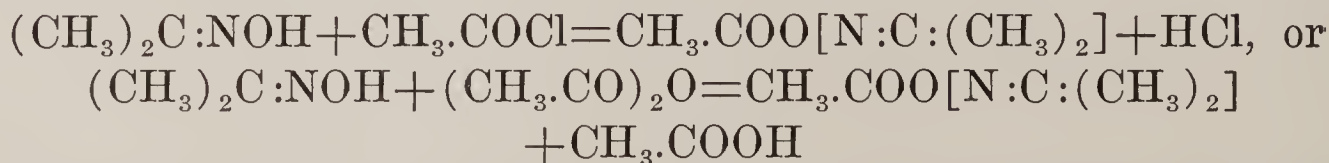
These reactions constitute a general method for obtaining amines (pp. 294, 296). Both aldoximes and ketoximes are hydrolyzed to their parent substances by boiling with acids:



The principal difference between aliphatic aldoximes and ketoximes is in their behavior towards acidyl halides and anhydrides, with which the former produce nitriles, and the latter esters. Thus with acetaldoxime:



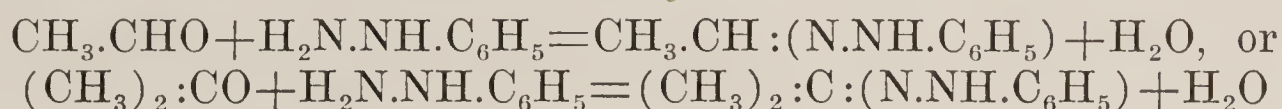
and with acetoxime:



Acetyl chloride and anhydride cause atomic rearrangement with

acyclic and some higher aliphatic ketoximes, to form phenyl or alkyl amides: $\text{C}_6\text{H}_5\text{CH}_3\text{C}:\text{NOH} = \text{C}_6\text{H}_5\text{CH}_3\text{CO}\text{NH}$.

Aldehyde hydrazones and **ketone hydrazones** are compounds corresponding to the aldoximes and ketoximes, formed by condensation of the aldehydes and ketones with phenylhydrazine (p. 379), the bivalent remainder of which, $=\text{N.NH.C}_6\text{H}_5$, is substituted for oxygen. They are obtained by the action of phenylhydrazine upon the aldehyde or ketone in ethereal solutions:



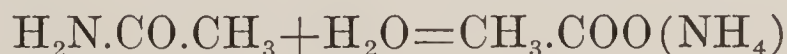
NITROGEN DERIVATIVES OF ACIDS.

The nitrogen derivatives of the pure carboxylic acids are numerous and varied. They may be divided into two classes: (1) Those in which nitrogen or a nitrogen-containing group is substituted in the carboxyl for OOH or for OH, and (2) those in which the substitution is in a hydrocarbon group. The first class includes the nitriles, amidines, hydroxamic acids, amidoximes, nitrolic acids and amides, which have already been considered, and the **hydrazides**, which are compounds bearing the same relation to the hydrazines (p. 302) that the amides do to the amines.

The following are included in the second class:

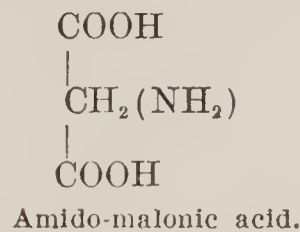
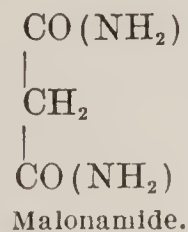
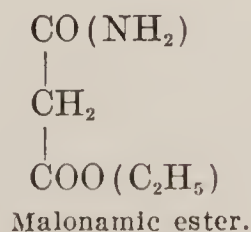
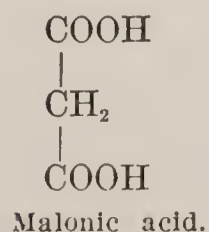
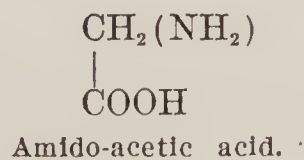
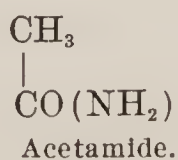
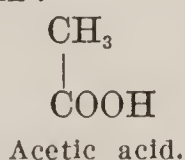
Nitro-acids, such as **nitro-acetic acid**, $\text{CH}_2(\text{NO}_2).\text{COOH}$, are unstable compounds, usually existing only in their esters and salts.

Monamido-acids are much more stable, and include a number of substances of physiological interest. They are derived from the fatty acids by substitution of one NH_2 for a hydrogen atom in a hydrocarbon group. In this position the attachment of the amido group is much firmer than it is in the primary monamides in which it replaces the hydroxyl. The amides are easily converted into ammonium salts by boiling water:

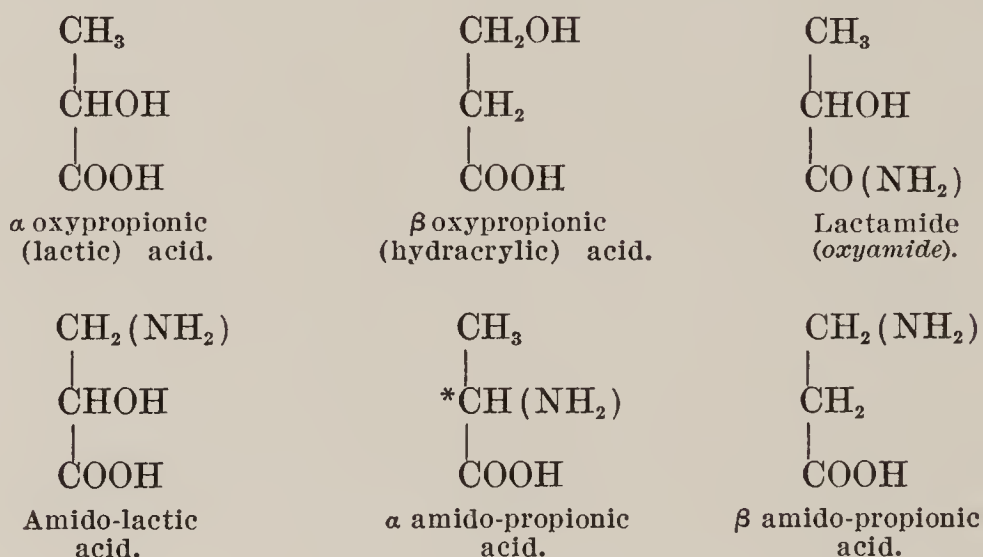


while the amido acids are not acted upon.

From the pure carboxylic acids, amic acids (p. 313), or amides (p. 311) amido-acids are derivable by substitution of HN_2 for OH or for H:



From the monocarboxylic oxyacids, **oxyamides** are derived by substitution of NH_2 for OH in COOH ; amido-acids of the same series by its substitution for H in a hydrocarbon group; and amido-acids of the acetic series by its substitution for OH in a CHOH or a CH_2OH group:

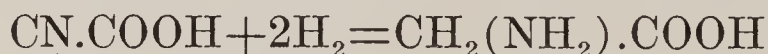


The first amido-acid of the fatty series, **amido-formic acid**, NH_2COOH , is carbamic acid. The third and superior terms of the series form place isomeres, according to the position of the NH_2 group, corresponding to the oxyacids and similarly designated as α , β , γ , etc., or 1-, 2-, 3-, etc. Those acids in which the NH_2 is not attached to the terminal C atom contain an asymmetric C^* , and therefore exist in optical isomeres. The fatty amido-acids are also known as **glycocolls** or **alanines**. They are obtained: (1) By the action of ammonia upon the monochloro acids. Thus amido-acetic acid is obtained from monochloroacetic acid:

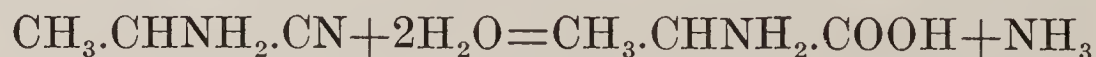


(2) By reduction of the nitro acids. Thus nitroacetic ester, $\text{CH}_2(\text{NO}_2).\text{COO.C}_2\text{H}_5$, yields amido-acetic ester.

(3) By the action of nascent hydrogen upon the cyan-fatty acids:



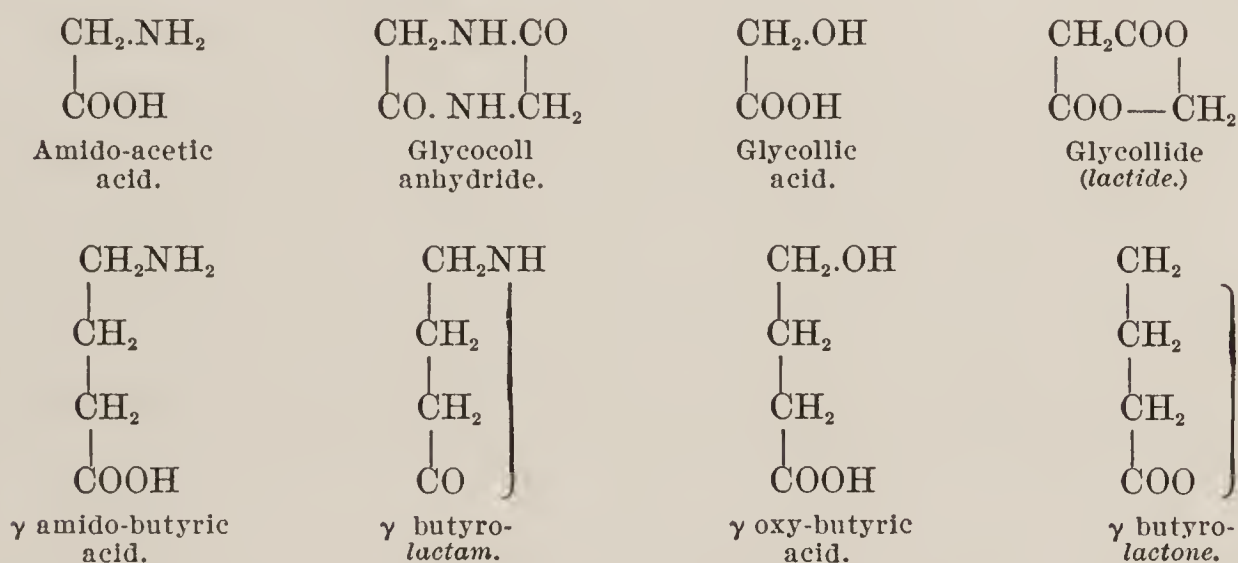
(4) By hydrolysis by HCl of the nitriles of the α amido-acids:



This method permits of the formation of the amido-acids from the corresponding alcohols, through the aldehydes.

The amido-acids are crystalline solids, most of which are sweet in taste, soluble in water, insoluble in alcohol or in ether, neutral in reaction. As they contain both amido and carboxyl groups, they have both basic and acid functions. With acids they form ammonium salts. They form stable metallic salts with bases, but their esters are unstable. The esters retain their basic function and form more stable hydrochlorides. Stable compounds are, however, produced by

the replacement of their amido hydrogen, either by acidyls or by alkyls. The acidyl compounds, such as **acetyl amido-acetic acid**, $\text{CH}_2\text{NH}(\text{C}_2\text{H}_3\text{O}).\text{COOH}$, are formed by the action of acidyl chlorides upon the amido-acids; and the alkyl derivatives, such as **methyl glycocoll**, $\text{CH}_2\text{NH}(\text{CH}_3).\text{COOH}$, by the action of amines upon haloid fatty acids. On dehydration the amido-acids behave like the oxyacids, which are also both basic and acid. The α acids on dehydration yield cyclic anhydrides, which are ketopiperazines and which on hydration yield, not two molecules of the acid, but a dipeptide. The γ and δ acids yield cyclic esters, called **lactams**, corresponding to the lactones. The resemblance of these compounds is shown by the following formulæ:

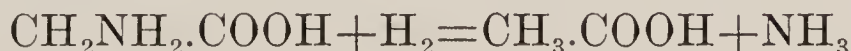


The formation of the lactams is another instance of the production of closed chain from open chain compounds.

By dry distillation the amido acids are split to amines and carbon dioxide:



When heated with hydriodic acid at 200° they are reduced to fatty acids:



Amido acids of the acetic and oxalic series are converted into the corresponding monochlor acid by nitrosyl chloride:



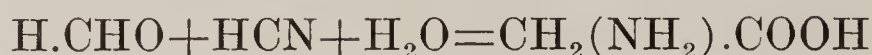
Nitrous acid acts upon the α -amido acids according to the reaction characteristic of the amido group converting them into oxyacids, with evolution of free nitrogen:



This conversion of amido into oxyacids, which probably occurs in the animal organism, is referred to as **deamidation**.

Amido-acetic Acid—Glycocoll—Glycine—Glycolamic acid—Gelatin sugar— $\text{CH}_2\text{NH}_2.\text{COOH}$ —was first obtained by the action of

H_2SO_4 upon gelatin. It is formed by the action of KOH upon glue; and, synthetically, by the methods given above and by the union of formic aldehyde, hydrocyanic acid and water:



It is produced along with benzoic acid, in the decomposition of hippuric acid (p. 375); as a product of decomposition of glycocholic acid; and by the action of hydriodic acid upon uric acid (p. 406). It occurs uncombined in the muscle of the scallop.

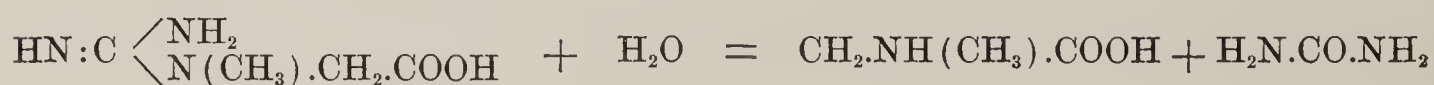
It appears as large, colorless, transparent crystals; has a sweet taste; fuses at 170° ; sparingly soluble in cold water; much more soluble in warm water; insoluble in absolute alcohol and in ether.

It forms crystalline salts with acids, which are decomposed at a boiling temperature. Nitric acid oxidizes it to glycollic acid. It is very resistant to oxidation by KMnO_4 in acid solution, but in alkaline solution or in its esters it is readily oxidized to urea:



from which it is presumed that the free acid does not exist as such, but as a lactam. Its acid function is more marked; it expels carbonic and acetic acids from calcium carbonate and lead acetate. It dissolves cupric hydroxide in alkaline solution, and there is no reduction on boiling the solution; but on addition of alcohol to the cold solution, blue crystalline needles of copper glycolamate separate. With ferric chloride it gives an intense red color, which is discharged by acids, and restored by ammonia. With phenol and sodium hypochlorite it gives a blue color, as does ammonia. It forms esters and amides. Its methylic ester is isomeric with sarcosine. Heated under pressure with benzoic acid it forms hippuric acid. Fused with urea it forms glycolylurea and, ultimately, uric acid.

Methyl-glycocoll—Sarcosine— $\text{CH}_2.\text{NH}(\text{CH}_3).\text{COOH}$ — isomeric with alanine, the methyl ester of glycocoll, and lactamide, is not known to exist as such in animal nature, but it may be obtained from creatine by the action of barium hydroxide:



It is formed by the action of methylamine upon monochloroacetic acid:

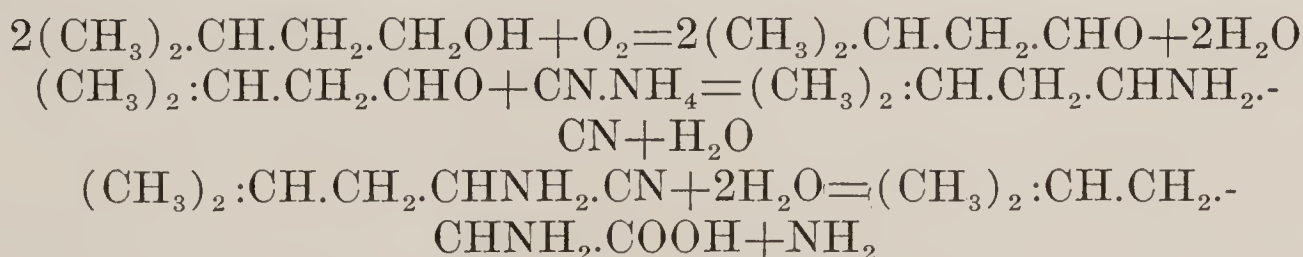


It crystallizes in colorless, transparent prisms; very soluble in water; sparingly soluble in alcohol and ether. Its aqueous solution is not acid, and has a sweetish taste. It forms salts with acids, but it is not known to form metallic salts. It unites with cyanamide to form creatine; and with cyanogen chloride to form methylhydantoïne.

Amido-propionic Acids—Alanines—Two are known: α alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, formed by the reduction of α nitroso-propionic acid; and β alanine, $\text{CH}_2(\text{NH}_2)\text{CH}_2\text{COOH}$, formed either by the reduction of β nitroso-propionic acid, or by the action of ammonia upon β iodo-propionic acid. Neither is known to exist in nature. Nitrous acid converts the two alanines into the corresponding lactic acids.

Amido-butyric Acids — $\text{C}_4\text{H}_9\text{NO}_2$ —and **Amido-valeric acids** — $\text{C}_5\text{H}_{11}\text{NO}_2$ — are mainly of theoretic interest. **Alpha amido-n-valeric acid**, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, is a product of oxidation of conine. **Alpha amido-iso-valeric acid—Butalanine**, $(\text{CH}_3)_2\text{CH}\text{CHNH}_2\text{COOH}$ occurs in the pancreas, and is formed as a product of decomposition of fibrin and of certain proteins.

Amido-caproic Acids—Leucines.—Twenty-seven isomeric amido acids are derivable from the seven caproic acids; and this number is still further increased by the fact that in many of these the introduction of the amido group renders a carbon atom asymmetric (see formula of α amido-propionic acid, p. 322). The leucine, which is of physiological interest as a product of decomposition of the proteins, is the *lævo* α amido-isobutyl-acetic acid, $(\text{CH}_3)_2\text{CH}\text{CH}_2\text{*CH}(\text{NH}_2)\text{COOH}$, as is demonstrated by its synthetic formation from isovaleric aldehyde, $(\text{CH}_3)_2\text{CH}\text{CH}_2\text{CHO}$:



The corresponding dextro-acid has been obtained by the action of *Penicillium glaucum* upon the inactive acid; and the *lævo*-acid, known as “vegetable leucine” from the vegetable globulin, conglutin.

d-isoleucine — methyl-ethyl- α -amido propionic acid — $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array} \text{CH}\text{CHNH}_2\text{COOH}$ — is also a product of hydrolysis of proteins, and is formed synthetically by the same methods as leucine, starting with secondary butyl carbinol $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array} \text{CH}\text{CH}_2\text{OH}$.

“Animal leucine” is produced, accompanied by tyrosine, in the decomposition of proteins by boiling with dilute acids or alkalies, by fusion with caustic alkalies, by putrefaction, and by trypsin digestion. It appears to exist also as a normal constituent of the pancreas, spleen, thymus, lymphatic and salivary glands, liver and kidneys. Pathologically the quantity of leucine is much increased in the liver in diseases of that organ, in typhus and in variola; in the bile in typhus; in the blood in leukemia, and in yellow atrophy of the liver; in the urine in yellow atrophy of the liver, in typhus, in variola, and in phosphorus poisoning; in choleraic discharges from the intestine; in pus; in the fluids of dropsy and of atheromatous cysts.

Leucine crystallizes from alcohol in soft, pearly plates, lighter than water, and somewhat resembling cholesterol; sometimes in

rounded masses of closely grouped, radiating needles. Pure leucine is sparingly soluble in water, almost insoluble in alcohol and ether, but readily soluble in hot water or alcohol. When impure it is more soluble. It is odorless and tasteless, and its solutions are neutral. It dissolves readily in acids and alkalis, forming crystalline compounds with the former. It fuses and sublimes at 170° without decomposition, but at a slightly higher temperature is decomposed into amylamine and carbon dioxide.

When heated with hydriodic acid under pressure the leucines are decomposed into ammonia and the corresponding caproic acids. By nitrous acid they are oxidized to the corresponding **oxycaproic**, or **leucic acids**, $C_6H_{12}O_3$, with elimination of water and of nitrogen. Hot solutions of leucine form precipitates with hot solutions of cupric acetate. They dissolve cupric hydroxide, but do not reduce it on boiling. When boiled with solution of neutral lead acetate and carefully neutralized with ammonia, they deposit brilliant crystals of a compound of leucine and lead oxide. When HNO_3 is slowly evaporated in contact with leucine on platinum foil a colorless residue remains, which, when warmed with NaOH solution, turns yellow or brown, and on further concentration, forms oily drops, which do not adhere to the platinum (Scherer's reaction). Solution of leucine, when heated with solution of mercurous nitrate, liberates metallic mercury (Hofmeister's reaction).

PHOSPHORUS, ANTIMONY, AND ARSENIC DERIVATIVES.

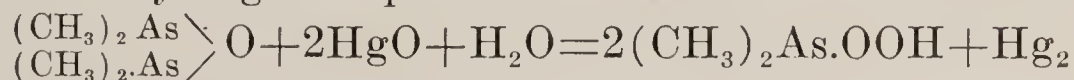
Many organic compounds, similar to those containing nitrogen, in which that element is replaced by phosphorus, antimony, or arsenic, are known. Of these only a few arsenic derivatives require mention.

Dimethyl Arsine — $(CH_3)_2HAs$ — corresponding to dimethyl amine, $(CH_3)_2HN$, is a colorless liquid, having an intensely disagreeable odor, which ignites spontaneously in air. It may be considered as the hydride of a radical, $(CH_3)_2As$, which, from the disagreeable odor and intensely poisonous action of all of its compounds, has received the name **cacodyl**. As the amines are considered as derived from ammonia by substitution of alkyl groups for the hydrogen, so the compounds of which this is a type are derived from the corresponding hydrogen compounds of phosphorus, antimony, and arsenic, and are called **phosphines**, **stibines**, and **arsines**.

The parent substance of the arseno-organic compounds is a fuming, foul-smelling liquid, obtained by distilling a mixture of arsenic trioxide and potassium acetate, and called **fuming liquid of Cadet**. The principal constituent of this is **cacodyl oxide**, or **alkarsine**, $(CH_3)_2As \backslash O$, a liquid which boils at 120° , insoluble in water, soluble in alcohol and in ether. **Cacodyl**, or **dicacodyl**, $(CH_3)_2As \cdot As(CH_3)_2$ is a colorless, insoluble liquid, which boils at 170° and

ignites spontaneously in air. Cacodyl and most of its compounds are exceedingly poisonous, especially the **cyanide** $(\text{CH}_3)_2\text{As}(\text{CN})$, an ethereal, volatile liquid the presence of whose vapor in air, even in minute traces, produces symptoms referable both to arsenic and to cyanogen. Probably minute quantities of arsines are formed during the putrefaction of cadavers embalmed with arsenical liquids.

Cacodylic acid $(\text{CH}_3)_2\text{As.O.OH}$. is formed by oxidation of cacodyl oxide by HgO in presence of water:



It is easily soluble in water; it is acid, odorless, and crystallizes in prisms. It is not attacked by nitric acid or even by aqua regia. Its salts are soluble in water and crystallize with difficulty. Its Na salt is used in medicine.

UNSATURATED ALIPHATIC COMPOUNDS.

In this class are included all open chain carbon compounds in which two carbon atoms exchange more than one valence (p. 197). As the saturated compounds consist of the members of the first, or methane, series of hydrocarbons and their derivatives, so the unsaturated compounds are the remaining series of open chain hydrocarbons and their unsaturated derivatives (p. 201).

HYDROCARBONS, ETHENE, OR OLEFINE SERIES.

The members of this series contain two atoms of carbon less than the corresponding terms of the methane series. They may be modified by addition, behaving as bivalent radicals, as well as by substitution. Their "Geneva" names terminate in **ene**.

Ethene—Ethylene—Olefiant gas—Olefine—Elayl— $\text{CH}_2:\text{CH}_2$ —is formed by the dry distillation of fats, resins, wood, and coal, and is a valuable constituent of illuminating gas.

It is formed synthetically: (1) By heating a mixture of alcohol, H_2SO_4 and sand. In this reaction ethyl-sulphuric acid is formed and decomposed:



(2) By the action of caustic potash upon ethyl bromide:



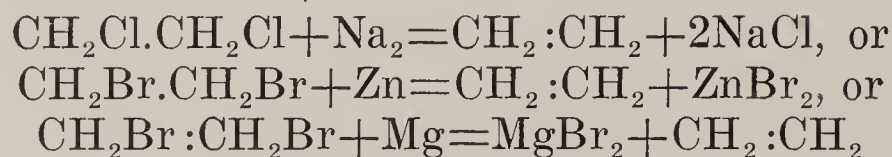
(3) By heating together acetylene and hydrogen, or by the action of nascent hydrogen upon copper acetylide:



(4) By heating methylene iodide with copper:



(5) By the action of sodium, of zinc or of magnesium upon ethylene bichloride or bibromide:

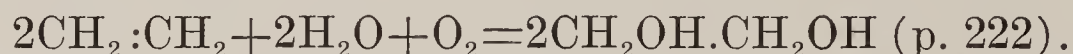


It is a colorless gas, tasteless, has a faint odor of salt water, sparingly soluble in water. Its critical temperature is 13° ; its critical pressure 60 atmospheres. It boils at -105° .

It burns with luminous flame, and forms explosive mixtures with air. By long contact with a red-hot surface it is decomposed into acetylene, methane, ethane, a tarry product, and carbon. It unites with hydrogen to form ethane, C_2H_6 ; with oxygen it unites explosively on approach of flame, to form carbon dioxide and water. It combines with hydrobromic and hydriodic acids to form ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$, and ethyl iodide, $\text{C}_2\text{H}_5\text{I}$. It combines with sulphuric acid to form ethyl-sulphuric acid: $\text{CH}_2:\text{CH}_2 + \text{H}_2\text{SO}_4 = \text{C}_2\text{H}_5.\text{HSO}_4$. Mixtures of ethene and chlorine explode, with copious deposition of carbon, on approach of flame. In diffuse daylight they unite slowly, with separation of an oily liquid, **ethylene chloride**, or **Dutch liquid**, $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$, to whose formation the name "olefiant gas" is due. The same compound is formed when ethene is passed through a mixture of MnO_2 , NaCl , H_2SO_4 , and H_2O . When passed through alkaline solution of potassium permanganate, it is oxidized to oxalic acid and water:



Or, by careful oxidation by dilute solution of the same agent, it forms ethene glycol:



When inhaled, diluted with air, ethene produces effects somewhat similar to those of nitrous oxide.

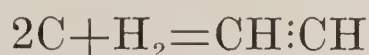
Two groupings of $(\text{C}_2\text{H}_4)''$ are possible,— $\text{CH}_2.\text{CH}_2$ —, and $\text{CH}_3.\text{CH}=\text{}$, the former produced by the breaking of the double bond between the carbon atoms in ethene, the latter by double substitution in ethane. Compounds containing the grouping— $\text{CH}_2.\text{CH}_2$ —are designated as **ethylene** or **ethene** compounds, *e.g.*, **ethylene chloride**, $\text{ClCH}_2.\text{CH}_2\text{Cl}$, b. p. 84° , those containing the grouping $\text{CH}_3.\text{CH}=\text{}$ are called **ethidene** or **ethylidene** compounds, *e.g.*, **ethidene chloride**, $\text{CH}_3.\text{CHCl}_2$, b. p. 58° .

Homologues of Ethene.—The superior homologues of ethene exist in coal gas and coal tar. They are formed by the methods 1 and 2, used for the preparation of ethene, but starting from the corresponding superior monoatomic alcohol. The lower terms are gaseous, the higher liquid at the ordinary temperature. They undergo reactions similar to those of ethene, and in addition, readily poly-

merize under the influence of sulphuric acid, zinc chloride and other substances.

ETHINE, OR ACETYLENE SERIES.

Acetylene—*Ethine*— $\text{HC}:\text{CH}$ —exists in coal gas, and is formed in the decomposition by heat or otherwise, of many organic substances. It is formed: (1) By passing an electric arc in an atmosphere of hydrogen:



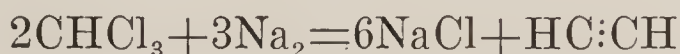
This is the only known synthesis of a hydrocarbon directly from the elements.

(2) By the action of water upon calcium carbide:

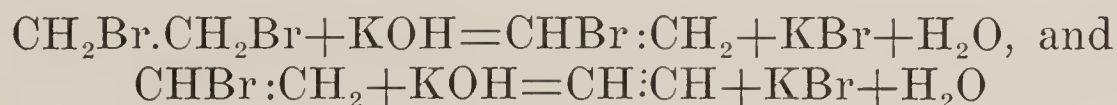


This method is used industrially for the preparation of acetylene for use as an illuminating gas.

(3) By heating chloroform, bromoform or iodoform with sodium, copper, silver or zinc:



(4) By heating ethylene bromide with caustic potash. The reaction occurs in two phases, vinyl bromide being formed as an intermediate product:



Acetylene is a colorless gas, rather soluble in water, having a peculiar, disagreeable odor, that which is observed when a Bunsen burner burns within the tube. This gas contains as impurities compounds of S, P, and Si, which must be removed if it is to be used indoors. It is liquefied by a pressure of 48 atmospheres at 0° . It forms explosive mixtures with air or oxygen. In contact with a red-hot surface, and in absence of air, it polymerizes to benzene $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$, an action which accounts for the presence of benzene in gas tar, and which is of great interest in connection with the relations between the open chain and the closed compounds. Nascent hydrogen converts acetylene into ethene, C_2H_4 , and then into ethane, C_2H_6 . Under the influence of the electric discharge, it combines with nitrogen to form hydrocyanic acid: $\text{C}_2\text{H}_2 + \text{N}_2 = 2\text{CNH}$. It combines with HCl and with HI to form ethidene chloride, $\text{CH}_3.\text{CHCl}_2$, or iodide, $\text{CH}_3.\text{CHI}_2$. Mixed with chlorine it detonates violently in diffuse daylight. The hydrogen atoms of acetylene may be replaced by metals to form **acetylides**, or **carbides**. **Sodium** and **calcium acetylides** are stable at high temperatures, but are decomposed by water with formation of acetylene. **Silver** and **copper acetylides** are highly explosive when dry, and explosions which have occurred when illumi-

nating gas was in contact with brass or copper were probably due to the formation of the latter. The formation of copper acetylide, which separates as a blood-red precipitate when acetylene is conducted through a solution of cuprous chloride, is utilized as a test for the presence of acetylene. Acetylene mercuric chloride, $C_2(HgCl)_2$, separates as a non-explosive, white precipitate when acetylene is passed through a solution of mercuric chloride.

DIOLEFINE AND SUPERIOR SERIES.

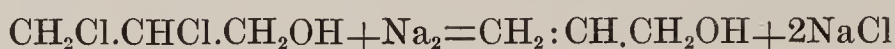
The **diolefines** are isomeric with the hydrocarbons of the acetylene series, containing two double linkages, in place of one triple linkage. Thus **allene**, or **allylene**, $CH_2:C:CH_2$, is isomeric with **propine**, or **propylene**, $CH:C.CH_3$.

Trimethyl-ethylene—Pentene—Amylene—Valerene— $(CH_3)_2:C:CH.CH_3$ —is a colorless, mobile liquid, boiling at 39° , obtained by heating alcohol with a concentrated solution of zinc chloride. It is used as an anesthetic, and in the preparation of tertiary amylic alcohol.

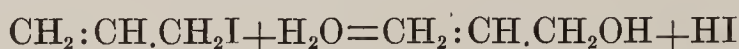
UNSATURATED OXIDATION PRODUCTS OF UNSATURATED HYDROCARBONS.

Like the paraffins, the olefines, acetylenes, diolefines, etc., yield alcohols, aldehydes, ketones, acids, oxides, and esters.

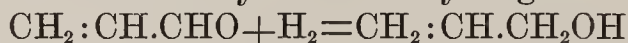
Allyl Alcohol— $CH_2:CH.CH_2OH$ —is formed: (1) By the action of sodium upon dichlorhydrine:



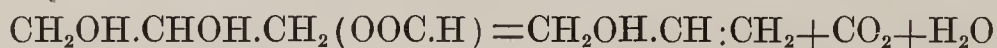
(2) By heating allyl iodide with water:



(3) By reduction of acrolein by nascent hydrogen:



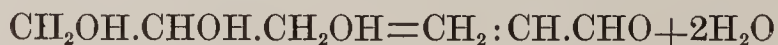
(4) By heating glycerol with formic acid, which first forms a glycerol ester, which then splits to allylic alcohol, carbon dioxide and water:



Oxalic acid, which yields formic acid, may be used in place of the latter.

It is a colorless, mobile liquid, solidifies at -50° , boils at 97° , sp. gr. 0.8507 at 25° , soluble in water, has an odor resembling the combined odors of alcohol and essence of mustard, burns with a luminous flame. It is isomeric with propylic aldehyde and with acetone. Oxidizing agents, such as silver oxide, convert it first into the corresponding aldehyde, **acroleine**, then into the acid, **acrylic acid**. It does not unite readily with hydrogen, but, in presence of nascent H, union takes place slowly, with formation of normal propyl alcohol. It forms products of addition with chlorine, bromine, and iodine, similar to those derived from glycerol.

Acrylic Aldehyde—Acroleine— $CH_2:CH.CHO$ —the first of the series of **olefine aldehydes**, is the substance which causes the disagreeable odor developed when fats or oils are overheated. It is formed: (1) By oxidation of allylic alcohol; (2) by distilling glycerol with strong H_2SO_4 or with $KHSO_4$:

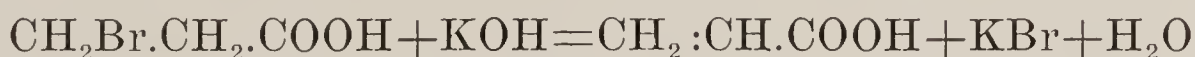


Acroleine is a colorless liquid, having a pungent odor, and giving off a vapor which is intensely irritating; sp. gr. 0.841 at 20° , boils at 52° , soluble

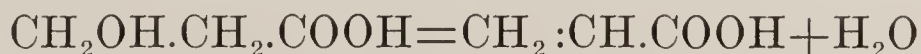
in 2–3 parts of water. Oxidizing agents convert it into acrylic acid. Nascent hydrogen reduces it to allyl alcohol. It does not combine with alkaline bisulphites. It reduces ammoniacal silver nitrate solution as does acetic aldehyde. It suffers change even when kept in closed vessels, and deposits a white, flocculent material, which is called **disacryl**, while formic, acetic and acrylic acids are also produced.

Oleic Acids.—The acids of this series are monocarboxylic acids derived from the olefines, and contain two atoms of hydrogen less than the corresponding terms of the acetic series. They are formed: (1) By oxidation of their corresponding alcohols or aldehydes. Thus allylic alcohol, $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$, or acroleine, $\text{CH}_2:\text{CH}.\text{CHO}$, yields acrylic acid, $\text{CH}_2:\text{CH}.\text{COOH}$.

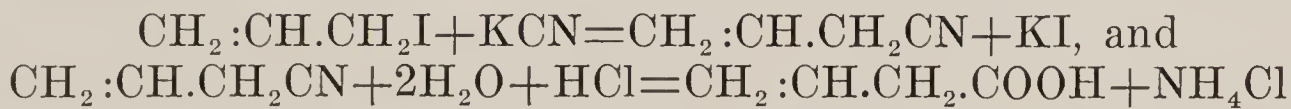
(2) By the action of alcoholic KOH upon the monohalogen fatty acids. Thus β monobromo propionic acid yields acrylic acid:



(3) By dehydration of acids of the oxyacetic series. Thus ethylene lactic acid forms acrylic acid when heated:



(4) From the allyl halides, by conversion into cyanides and saponification. Thus crotonic acid is obtained from allyl iodide:



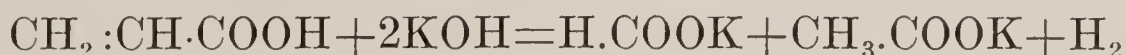
The oleic acids combine with the hydracids to form monohalogen fatty acids, the halogen assuming the position furthest removed from the carboxyl. Thus acrylic acid and hydriodic acid form β iodo propionic acid:



Heated with caustic alkalies to 100° , they form oxyacids. Thus acrylic acid forms α lactic acid:



But, when fused with caustic alkalies, they are decomposed into fatty acids, with loss of H. Thus acrylic acid yields formic and acetic acids:



The $\beta\gamma$ acids, *i.e.*, those in which the double bond is between the β and γ positions, as in **ethidene propionic acid**, $\text{CH}_3.\text{CH}:\text{CH}.\text{CH}_2.\text{COOH}$, when heated with H_2SO_4 form lactones.

Acrylic Acid— $\text{CH}_2:\text{CH}.\text{COOH}$ —is best obtained by oxidizing acroleine with silver oxide. It is a liquid below 7° , boils at 140° , mixes with water, and has an odor like that of acetic acid.

Oleic Acid— $\text{CH}_3.(\text{CH}_2)_7.\text{CH}:\text{CH}.\text{CH}_2.\text{COOH}$ —exists as its glyceric ester in fats and fixed oils, and is obtained in an impure

form, on a large scale, as a by-product in the manufacture of stearin candles.

Pure oleic acid is a white, pearly, crystalline solid, fuses at 14° , odorless, tasteless, soluble in alcohol and in ether, insoluble in water, sp. gr. 0.808 at 19° , and neutral in reaction. Exposed to air, the liquid acid absorbs oxygen, and becomes yellow, rancid in taste and odor, acid in reaction, and incapable of solidification on cooling. Nitric acid oxidizes it, with formation of the lower fatty acids and **sebacic acid**, $C_{10}H_{18}O_4$. Heated to 200° with excess of caustic potash, it is split into palmitic and acetic acids:



The oleates of the alkaline metals are soft, soluble soaps; those of the earthy metals are insoluble in water. The action of iodine and of bromine upon oleic acid is utilized in the analysis of fats and oils. At the ordinary temperature the fatty acids, including palmitic and stearic, are not affected by iodine, but the double bond in oleic acid is broken, and one molecule of oleic acid combines with two atoms of iodine. Under like conditions each molecule of linoleic acid takes up four atoms of iodine. The amount of iodine which a given weight of a fat or oil can combine with will increase with its tenure of oleic, or, particularly, of linoleic acid. "Hubl's iodine number" of a fat or oil is the quantity of iodine which 100 grams of the substance can take up under the conditions of the process and is an important factor for its identification.

Elaidic Acid— $C_{17}H_{33}.COOH$ —is an isomere of oleic acid, produced from it by the action of nitrous acid. It is a crystalline solid, fusible at 51° . Its formation is utilized to distinguish non-drying from drying oils (p. 282). The former, containing oleic acid, solidify when acted on by nitrous acid; the latter, containing linoleic acid, do not.

Olefine dicarboxylic Acids.—The acids of this series contain two atoms of hydrogen less than the corresponding acids of the oxalic series, and they consequently bear the same relation to those acids that the acids of the oleic series bear to those of the acetic series.

Esters of three acids having the composition $C_2H_2(COOH)_2$ are known. The free acid corresponding to one of these, **methylene malonic ester**, $CH_2:C \begin{smallmatrix} \diagup COO(C_2H_5) \\ \diagdown COO(C_2H_5) \end{smallmatrix}$, is not known. The other two, **fumaric** and **maleïc acids**, are "space isomerides" (p. 238). **Fumaric acid** is considered to have the axial

symmetric structure:
$$\begin{array}{c} H.C.OOH \\ || \\ HOOC.C.H \end{array}$$
, because it does not yield an anhydride,

and because, on oxidation, it yields racemic acid, while **maleïc acid** has the plane symmetrical structure, because, owing to the closer proximity of the carboxyls,

$$\begin{array}{c} H.C.COOH \\ || \\ H.C.COOH \end{array}$$
, it readily forms an anhydride,
$$\begin{array}{c} H.C.CO \backslash \\ || \\ H.C.CO / \end{array} O$$
, and because on oxidation

it yields inactive, or meso-tartaric acid (see p. 239 and Fig. 18, *ibid.*).

Fumaric acid exists free in many plants, notably in Iceland moss. Fumaric and maleïc acids are readily converted one into the other by simple heating,

and the two are produced together by the action of heat upon malic acid, or by boiling solutions of monobromo-succinic acid.

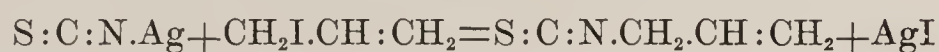
Fumaric acid crystallizes in small prisms, almost insoluble in cold water, which sublimes at 200° . Maleïc acid fuses at 130° , and boils at 160° . Both fumaric and maleïc acids are converted into succinic acid by nascent hydrogen.

Allyl Oxide—*Allylic ether*— $(\text{CH}_2:\text{CH}.\text{CH}_2)_2\text{O}$ —is an example of the unsaturated ethers. It exists in small quantity in crude essence of garlic, and is formed by the action of allyl iodide upon sodium-allyl oxide. It is a colorless liquid, having the odor of garlic, insoluble in water, boiling at 82° . Mixed ethers are also known, such as **propargyl ethyl ether**, $\text{CH}:\text{C}.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_3$.

UNSATURATED SULPHUR AND NITROGEN COMPOUNDS.

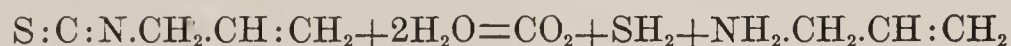
Allyl Sulphide— $(\text{CH}_2:\text{CH}.\text{CH}_2)_2\text{S}$ —corresponding to the oxide, is the principal constituent of volatile oil of garlic, obtained by distilling garlic with water. It is formed by the action of alcoholic solution of potassium sulphide upon allyl iodide. It is a colorless oil, lighter than water, soluble in alcohol and in ether, boils at 140° .

Allyl Isothiocyanate—*Mustard oil*— $\text{S}:\text{C}:\text{N}.\text{CH}_2.\text{CH}:\text{CH}_2$ —is the chief constituent of volatile oil of mustard, and of radish oil. It is prepared artificially by distilling allyl bromide or iodide with potassium or silver thiocyanate:



It does not exist preformed in the mustard seeds, but is produced by the decomposition of a glucoside, **potassium myronate**, in the presence of water under the influence of an enzyme, also contained in the seeds, called **myrosin**. The action takes place at 0° , but not at temperatures above 40° . The activity of myrosin is also impaired by the presence of acetic acid (vinegar). The pungent, rubefacient and vesicant actions of mustard are due to mustard oil.

Pure allyl isothiocyanate is a colorless oil, sp. gr. 1.015 at 20° , boils at 150° , has a penetrating, pungent odor, sparingly soluble in water, very soluble in alcohol and in ether. Exposed to air it gradually turns brownish-yellow, and deposits a resinoid material. Heated with HCl or with H_2O , it is decomposed into carbon dioxide, hydrogen sulphide and **allyl-amine**:



CLOSED CHAIN, AROMATIC OR CYCLIC COMPOUNDS.

These compounds, which include many important natural products, and a practically unlimited number of synthetic compounds, differ from the members of the open chain series in that they contain a group of more than two atoms united together by exchange of valences in such a manner as to form a **closed chain**, or **ring**, or **nucleus**. If all the atoms so united are carbon atoms the substance belongs to the **carbocyclic** class; if an element other than carbon enters into the formation of the ring the substance is **heterocyclic**.

Some closed chain compounds are produced by the interaction of two open chain compounds, as in the formation of certain diamines (p. 296) and compound ureas (p. 316). Others, such as the lactides (p. 283), lactones (p. 283), and lactams (p. 323), are produced by internal reaction in an open chain molecule. But the principal method of formation of closed chain compounds is by polymerization. In some cases this takes place at comparatively low temperatures, as in the formation of trioxymethylene from formaldehyde (p. 228), and of the polymeric thioaldehydes and their sulphones (p. 284).

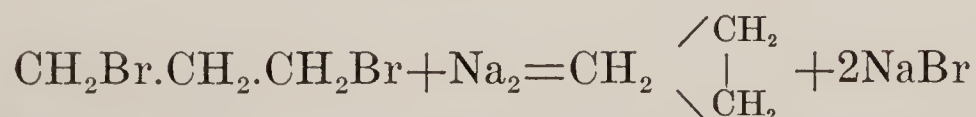
Among the instances of formation of cyclic from acyclic compounds there is one of polymerization at a high temperature which is of special interest as bearing upon the constitution of the cyclic compounds. The central figure of the carbocyclic compounds is **benzene**, C_6H_6 , which is obtained principally from gas-tar. Coal gas contains **acetylene**, C_2H_2 , and it is easy to conceive that one or two of the bonds uniting the two carbon atoms in acetylene may be loosened under the influence of heat, and that a molecule of benzene may be produced by fusion of three molecules of acetylene: $3C_2H_2 = C_6H_6$. The product so obtained is neither dipropargyl, $HC\equiv C\cdot CH_2\cdot CH_2\cdot C\equiv CH$, nor dimethyl diacetylene, $H_3C\cdot C\equiv C\cdot C\equiv C\cdot CH_3$, but another substance, the nature of whose substituted derivatives indicates that the six hydrogen atoms are of equal value, and therefore similarly attached to carbon atoms; and, there being three bisubstituted derivatives (p. 337), to at least three different carbon atoms. These conditions can only be fulfilled by a cyclic structure of the molecule of benzene and its derivatives (p. 336). Pyridine also, which has a prominence among the heterocyclic compounds corresponding to that of benzene among the carbocyclic, has been obtained from acetylene and hydrocyanic acid by a fusion very similar to that by which acetylene alone forms benzene: $2C_2H_2 + HCN = C_5H_5N$. It is also formed by the action of heat upon substances containing nitrogen as well as carbon.

CARBOCYCLIC COMPOUNDS.

Carbocyclic compounds are known containing from three to seven carbon atoms in a ring. Compounds are also known containing a much larger number of carbon atoms, but these are formed by fusion or union of two or more rings of six carbon atoms or less, or by the attachment of an open chain grouping upon a closed chain one (p. 340). The hexacarbocyclic compounds are far more numerous and important than the others.

The mononuclear carbocyclic hydrocarbons have algebraic formulæ varying from C_nH_{2n} to C_nH_{2n-6} , and are isomeric with the unsaturated open chain hydrocarbons (p. 201). Those of the series C_nH_{2n} are known as **polymethylenes**, being considered as formed by the union of a number of methylene groups, CH_2 . Thus **hexahydrobenzene** is **hexamethylene**, $CH_2 \begin{smallmatrix} \diagup CH_2.CH_2 \\ \diagdown CH_2.CH_2 \end{smallmatrix} CH_2$. But the chemical relations of the polymethylenes to the saturated hydrocarbons is closer than that to their isomeres, the olefines, because, containing no double linkages, they cannot be modified by addition without disruption of the ring. So long as the cyclic formation is maintained, the polymethylenes are saturated compounds, as are the paraffins. For this reason their "Geneva" names are the same as those of the paraffins of like carbon content, to which is prefixed the syllable "**cyclo**," and they are known generically as **cycloparaffins**; or the symbol R is used in place of the syllable "cyclo." The hydrocarbons of the series C_nH_{2n-2} , isomeric with the acetylenes and diolefines, are referable to the latter, not to the former, as they cannot contain a triple linkage in the ring. But, containing only one double linkage, they are more closely related to the olefines. Therefore **tetrahydrobenzene**, $CH \begin{smallmatrix} // CH.CH_2 \\ \diagdown CH_2.CH_2 \end{smallmatrix} CH_2$, isomeric with hexadiene, $CH_2:CH.CH_2.CH_2.CH:CH_2$, containing but one double linkage, is **cyclo-hexene**, or **R-hexene**. Similarly **dihydrobenzene**, $CH \begin{smallmatrix} \diagup CH_2.CH_2 \\ // CH.CH \end{smallmatrix} CH$, is a **cyclo-diolefine: R-hexadiene**; and benzene a **cyclotriolefine: R-hexatriene**.

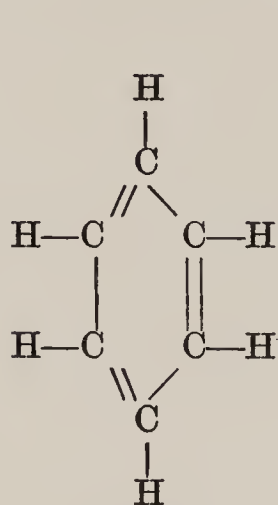
The cycloparaffins are formed by the action of sodium upon the dibromoparaffins. Thus trimethylene is obtained from trimethylene bromide:



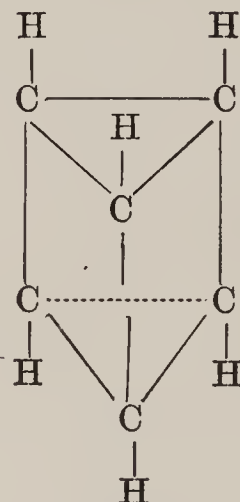
Tri-, tetra-, penta-, and hepta-carbocyclic hydrocarbons, and their numerous derivatives, notably acids and ketones, are known. They are not as yet, however, of medical interest, except that certain tetra-, and penta-compounds are among the decomposition products of certain alkaloids.

HEXACARBOCYCLIC COMPOUNDS—AROMATIC SUBSTANCES.

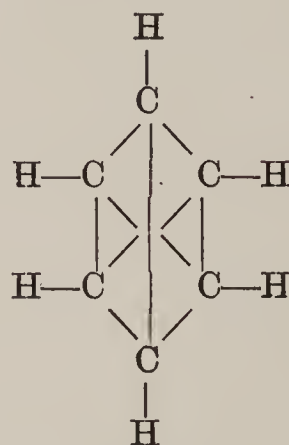
These compounds, which are very numerous and important, all contain a group of six carbon atoms, to which are attached six, eight, ten or twelve univalents, or their equivalent. As the simplest representative of the class is benzene, C_6H_6 , and as all of these bodies may be derived from benzene, directly or indirectly, and yield that hydrocarbon on decomposition, *the aromatic substances may be considered as derivatives of benzene*. This being the case, the constitution of benzene itself is of great importance, and has been the subject of much study. Several schematic representations of the structure of the benzene molecule have been suggested, the most demonstrative of which are the hexagonal form of Kekulé, the prismatic form of Ladenburg, and the diagonal form of Claus:



Hexagonal.



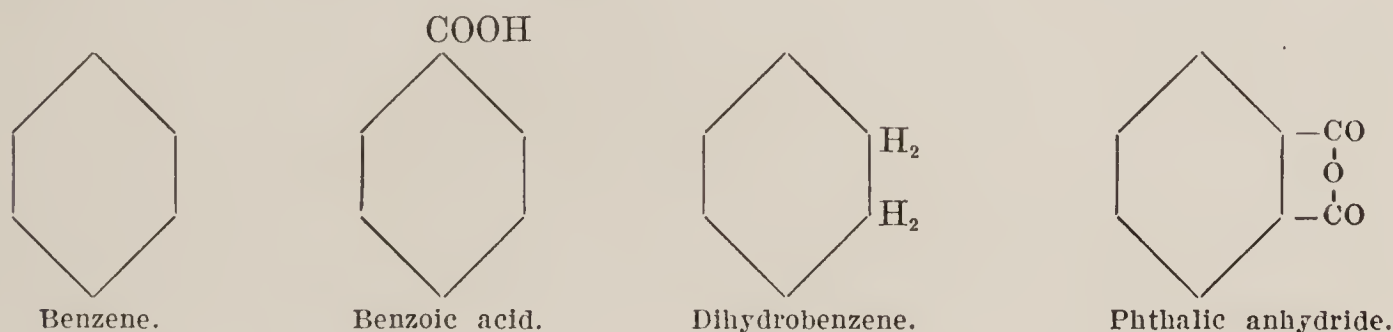
Prismatic.



Diagonal.

In the hexagonal formula the carbon atoms exchange one and two valences alternately, each being attached to two others; in the prismatic form each carbon atom is attached to three others by single valences; and in the diagonal form the hexagon is retained, but, in place of double linkages, a central linkage between all the carbon atoms is substituted. All of these formulæ represent the equivalence of the carbon atoms, and the constitution of isomeres equally well (see below). The prismatic formula cannot be modified to represent a constitution of the additive derivatives of benzene, such as dihydrobenzene, $CH \begin{smallmatrix} \diagup CH_2.CH_2 \\ \diagdown CH.CH \end{smallmatrix} CH$, and tetrahydrobenzene, $CH \begin{smallmatrix} \diagup CH_2.CH_2 \\ \diagdown CH.CH_2 \end{smallmatrix} CH_2$. Neither the prismatic nor the diagonal formula admits double linkages between carbon atoms in the ring. That these exist is shown, however, by the formation of the additive products mentioned, by the formation of anhydrides from ortho-derivatives only (see below), and by certain physical properties. Moreover, the hexagonal formula ac-

cords well with the tetrahedral representation of the valences of the carbon atom (p. 239), the six tetrahedra being alternately united by edges and apexes in benzene, and by apexes in hexahydrobenzene. For these (and other) reasons, chemists have very generally adopted the hexagonal expression, although it still leaves something to be desired. The figure of a hexagon is used in chemical writings to represent the benzene ring. If used alone it represents a molecule of benzene, C_6H_6 ; and to represent the products of substitution the symbols of the substituted group are written in the proper position, thus:



Isomerism of Benzene Substitution Products.—(1) *The six atoms of hydrogen in benzene are of equal value.* There exists but one mono-substituted derivative of benzene containing any given univalent: one chlorobenzene, C_6H_5Cl , one nitro-benzene, $C_6H_5(NO_2)$, one amido-benzene, $C_6H_5(NH_2)$, one benzoic acid, $C_6H_5.COOH$, etc. Therefore, benzene is symmetrical in structure, and its hydrogen atoms equal each other in value, as do those of methane, while those of pyridine (p. 000) are not all of like value.

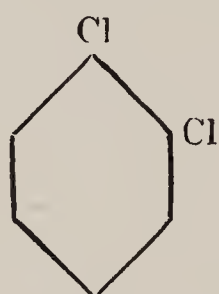
2. *Any hydrogen atom selected in the benzene ring is symmetrically placed in reference to two pairs of hydrogen atoms, and to the sixth hydrogen atom individually.* With all di-, tri-, and tetra-substituted derivatives of benzene, containing like substituted univalents, there are three isomeres. Three dichloro-, three trichloro-, and three tetrachloro-benzenes, etc., and in no instance are more than three known. There is but one explanation of the facts mentioned above, namely, that the different bi-, tri-, and tetra-derivatives are produced by differences in the relative positions of the substituted groups, by differences in “**orientation**,” as among the aliphatic compounds, the several oxyacids are “place isomeres” of each other (p. 260).



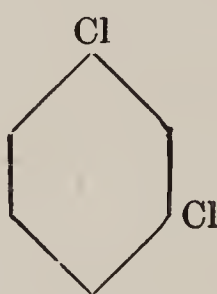
The hexagonal formula of benzene is very convenient for showing the structure of the several isomeres. For this purpose the carbon atoms are numbered, beginning, for convenience, at the top and proceeding clockwise.

It has been demonstrated that in some of the bisubstituted derivatives the two substituted groups are attached to **adjacent** carbon atoms, *i.e.*, to 1-2, 2-3, 3-4, 4-5, 5-6, or 6-1. Clearly for each carbon atom there is a pair of **adjacent positions**, as

1-2 and 1-6, 2-1 and 2-3, etc., which are equivalent to each other.* In other bisubstituted derivatives it may be shown that the two substituted groups are attached to carbon atoms, separated from each other by one carbon atom on one side and by three on the other, an arrangement which renders the hexagon **unsymmetrical**. Such positions are 1-3, 2-4, 3-5, 4-6, 5-1, and 6-2. Or, for each carbon atom there is a pair of equivalent unsymmetrical positions, as 1-3 and 1-5, etc. There remains but one other arrangement possible, the **symmetrical**, or diagonal, 1-4, 2-5, 3-6. With the tri- and tetra-substituted derivatives there are also three possible arrangements: the **adjacent**, **vicinal**, or **consecutive**, as 1-2-3, 2-3-4; 1-2-3-4, or 2-3-4-5; the **unsymmetrical**, as 1-2-4, 3-4-6; 1-2-3-5, or 3-4-5-1; and the **symmetrical**, as 1-3-5, 2-4-6; 1-2-4-5, or 3-4-6-1. Compounds in which the substitution is adjacent are designated as **ortho-compounds**, or, in writing, by the abbreviation o-, or by the figures 1-2, etc. Thus $\text{C}_6\text{H}_4(\text{OH})_{2(1-2)}$, o-diphenol. Unsymmetrical compounds are designated as **meta-compounds**, or, abbreviated, m-, or by the figures, 1-3, etc.; *e.g.*, $\text{C}_6\text{H}_3(\text{Br})_{3(1-2-4)}$, m-tribromobenzene. Symmetrical compounds are designated as **para-compounds**, abbreviated p-, or 1-4, etc.: *e.g.*, $\text{C}_6\text{H}_2(\text{NH}_2)_{4(1-2-4-5)}$, p-tetraamido-benzene. Or, to illustrate by the formulæ of the di- and tetra-chlorobenzenes:



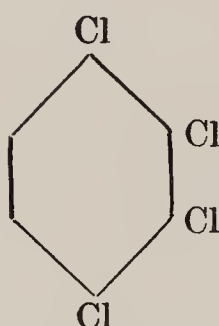
1-2



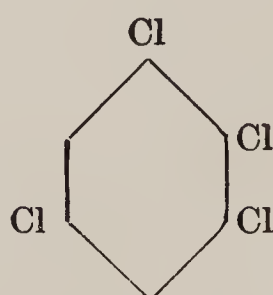
1-3



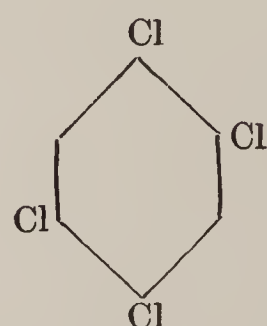
1-4



1-2-3-4

Adjacent.
Ortho.

1-2-3-5

Unsymmetrical.
Meta.

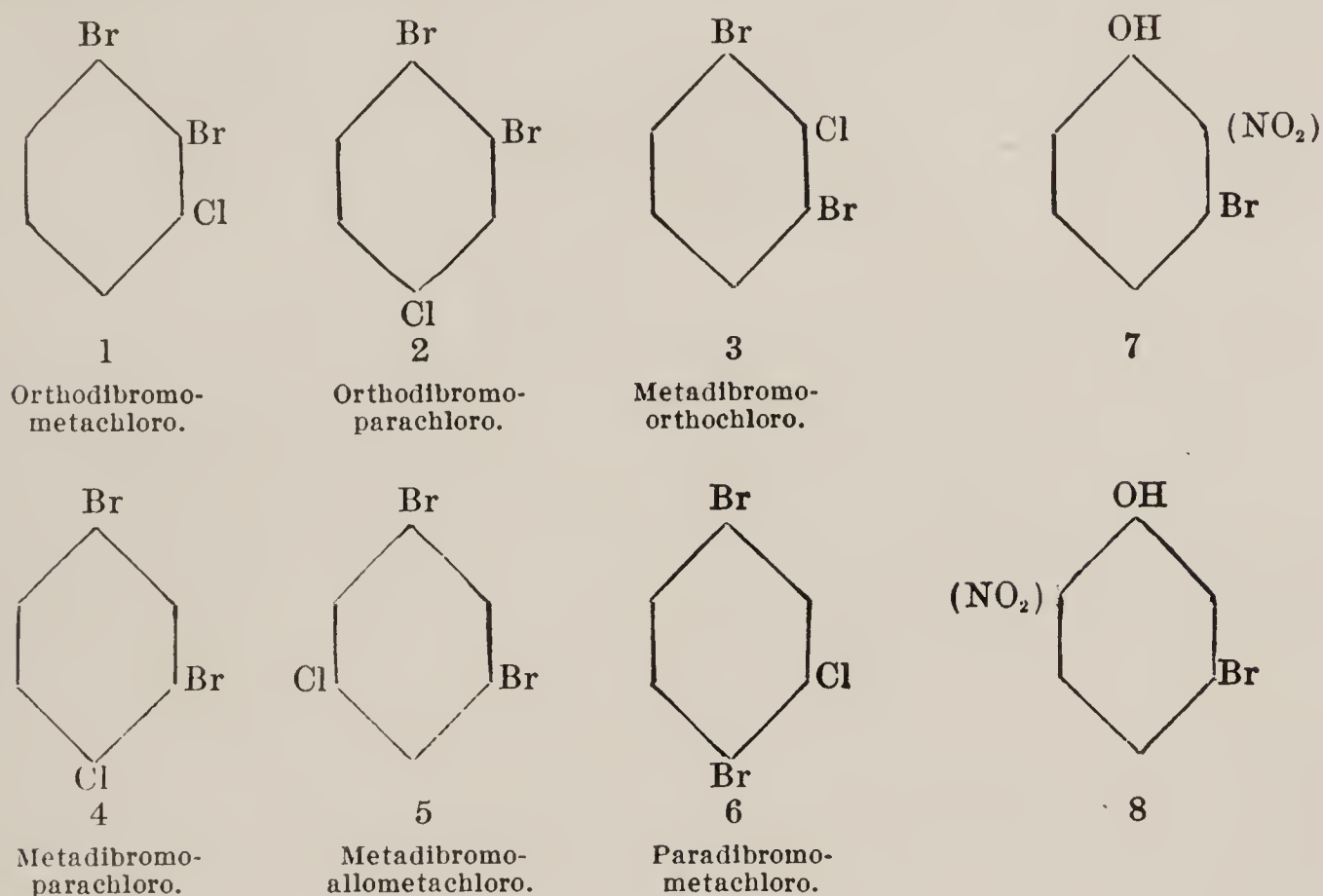
1-2-4-5

Symmetrical.
Para.

In the bisubstituted derivatives it is immaterial whether the two substituted groups are of the same kind or different. But when, in a trisubstituted derivative, the substituted groups are not the same

* Note.—The principal objection to the hexagonal formula of benzene (and stated by Kekulé himself) is that these two positions are not entirely equivalent, as in the position 1-2 the grouping is =C—C= , while in 1-6 it is —C=C— , and that consequently there should be two ortho derivatives, while but one is known. The student is referred to more extended works for a discussion of this subject.

in kind, the number of possible isomeres is increased. Thus there are six possible chloro-dibromobenzenes (formulae 1 to 6 below), of which two (1 and 2) are derived from orthodibromobenzene, $C_6H_4:Br_2$ (1, 2), three (3, 4, and 5) from metadibromobenzene, $C_6H_4:Br_2$ (1, 3), and one (6) from paradibromobenzene, $C_6H_4Br_2$ (1, 4). The number of possible trisubstituted derivatives is increased to ten when all three substituted groups are of different kind.



In naming these derivatives, the characterizing group of the parent substance is given the position 1 in the hexagon, the prefix “ortho” is applied to the name of the group occupying one of the ortho positions 2 and 6, “meta” to that occupying one of the meta positions 3 and 5, and “para” to that occupying the para position 4. Thus the substance having the formula 7 above is **orthonitro-meta-bromo-phenol**. But another substance is known, not identical with this, having the formula 8 above, in which the nitro group occupies the second ortho position, 6. To distinguish substances such as these, the designation “allortho” is given to the position 6, and the designation “allometa” to the position 5. Thus the substance having the formula 8 is **metabromo-allorthonitro-phenol**. When formulae are used the numerals corresponding to the position of substitution, enclosed in brackets, are placed after the symbols. Thus 7 is written: $C_6H_3(OH)(NO_2)_{[2]}Br_{[3]}$, and 8: $C_6H_3(OH)Br_{[3]}(NO_2)_{[6]}$.

Classification of Aromatic Substances.—The benzene derivatives may be classified into five classes:

A. Compounds containing a single benzene nucleus, unmodified except by substitution for hydrogen. Monobenzenic compounds. In-

cludes benzene and its homologues, and the phenols, alcohols, acids, etc., derived from them.

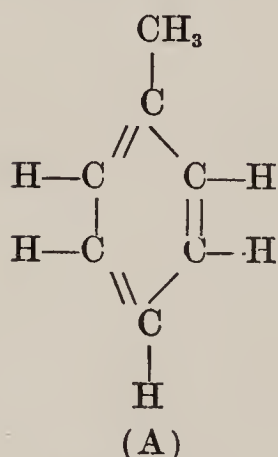
B. Compounds containing a single benzene nucleus in which one (or more) of the double bonds has been converted into a single one, thus adding two, four, or six valences to the carbon ring. Monohydrobenzenic compounds. Includes the cyclohexadienes, cyclohexenes, and cyclohexanes (p. 335), and their derivatives, among which are the terpenes and camphors.

C. Compounds containing two (or more) benzene nuclei, or benzene and pentacarbo-cyclic rings, fused together, and having two carbon atoms in common. Includes indene, fluorene, naphthalene, anthracene, and phenanthrene and their derivatives. Compounds with condensed nuclei.

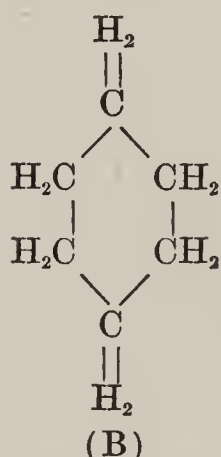
D. Compounds containing two (or more) benzene rings, directly united by loss of two H atoms. Diphenyl and its derivatives.

E. Compounds containing two (or more) benzene nuclei, united by aliphatic groups. Includes di- and polyphenyl paraffins, olefines and acetylenes and their derivatives.

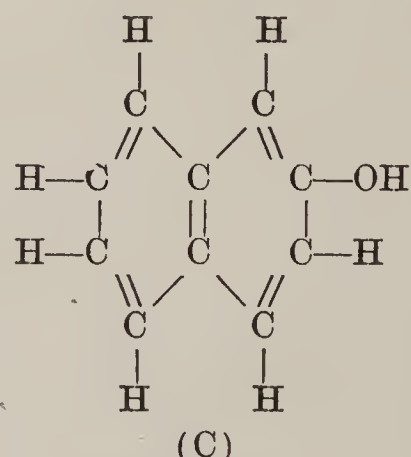
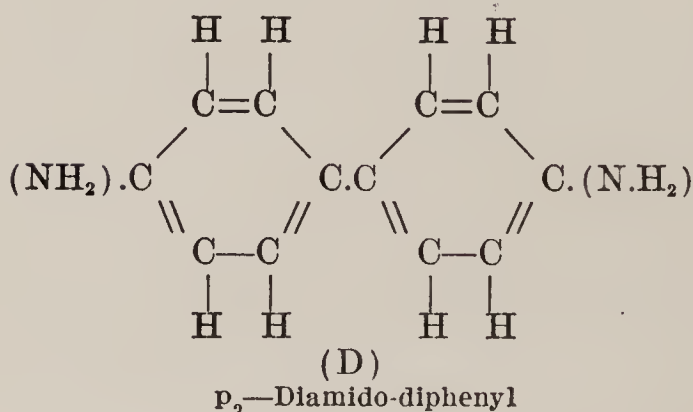
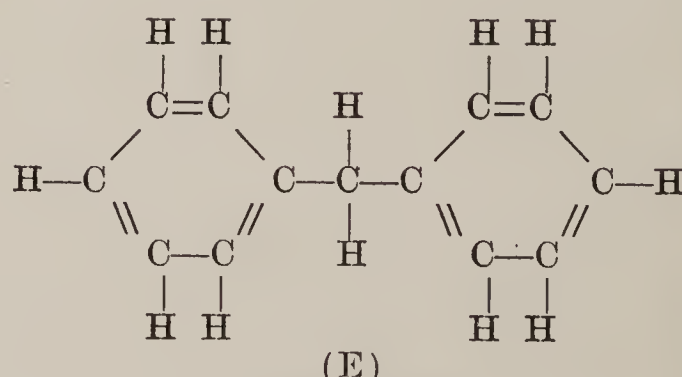
The following formulæ will serve to indicate the differences in constitution of the several classes:



Methyl-benzene.



Hexahydrobenzene.

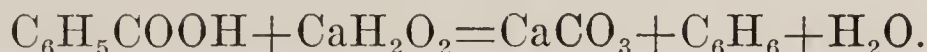
 β Naphthol. p_2 -Diamido-diphenyl

Diphenyl-methane.

A. MONOBENZENIC COMPOUNDS.

HYDROCARBONS.

Benzene—*Benzol*— C_6H_6 —(not to be confounded with *benzine*, a mixture of hydrocarbons of the series C_nH_{2n+2} , obtained from petroleum) does not exist in nature. It is obtained, pure, by decomposing benzoic acid by heating with slaked lime:



It is produced in the distillation of coal, and exists in coal tar, from which it is obtained for use in the arts.

Coal tar, or gas tar, is a very complex mixture, containing forty or fifty substances—hydrocarbons, phenols and bases—and is the crude material from which many important substances are obtained. In working it, it is first distilled, four fractions being collected: (1) *Light oil*, distilling below 150° ; (2) *carbolic oil*, or *middle oil*, distilling below 230° . Contains phenols and naphthalene. (3) *Heavy oil*, or *creosote oil*, distilling below 270° . Furnishes naphthalene. (4) *Green oil*, or *anthracene oil*, distilling above 270° . Contains anthracene and other solid hydrocarbons. The residue in the still is pitch. The light oil contains benzene, toluene and xylene, with some thiophene, phenols, pyridine, and heavy oils. It is further purified to yield various grades of commercial “*benzol*,” the best of which contains about 70 per cent. of benzene, and 24 per cent. of toluene, with some xylene, cumene and thiophene.

Pure benzene is a colorless liquid, having an ethereal odor, crystallizing at 5.4° , boiling at 80.5° , sp. gr. 0.86 at 15° , immiscible with water, mixing with alcohol and ether. It dissolves I, S, P, resins, caoutchouc, guttapercha, fats and many alkaloids. It is inflammable, and burns with a smoky flame.

Benzene unites directly with Cl or Br to form products of addition or of substitution. Free Cl acts only slowly upon benzene alone, but the action is much accelerated by the presence of certain chlorides, particularly $FeCl_3$. The corresponding I derivatives can only be obtained indirectly. Sulphuric acid combines with it to form **benzene sulphonic acid**, $C_6H_5.SO_3H$. Nitric acid converts it into nitro-benzene, $C_6H_5.NO_2$, or, if fuming HNO_3 is used and the mixture boiled, into a mixture of the three dinitro-benzenes, $C_6H_4(NO_2)_2$. It is reduced to hexahydrobenzene by hydriodic acid.

Homologues of Benzene.—These may be considered as alkyl-benzenes, formed by the substitution of alkyl groups for an equivalent number of hydrogen atoms in benzene. The usual general method of their formation indicates the constitution: they are obtained by treating a mixture of bromobenzene, ether,

HALOID DERIVATIVES.

By the substitution of atoms of Cl, Br and I for the hydrogen of the principal and lateral chains in benzene and its superior homologues, a great number of substances are obtained, many of them forming isomeric groups.

The chlorobenzenes are: **Monochlorobenzene**: C_6H_5Cl , liquid, b. p. 132° , sp. gr. at 0° —1.128 $^\circ$; obtained by the action of Cl upon C_6H_6 in the cold, in presence of a little I.

Orthodichlorobenzene: $C_6H_4Cl_2$ (1-2), liquid, b. p. 179° , sp. gr. 1.328 at 0° ; obtained by the action of Cl upon C_6H_6 .

Metadichlorobenzene: $C_6H_4Cl_2$ (1-3), liquid, b. p. 172° , sp. gr. 1.307 at 0° ; obtained indirectly.

Paradichlorobenzene: $C_6H_4Cl_2$ (1-4), crystalline, f. p. 56.4° , b. p. 170° , is the principal product of the action of Cl on C_6H_6 in presence of I.

Metatrichlorobenzene: $C_6H_3Cl_3$ (1-2-4), crystals, f. p. 17° , b. p. 213° .

Paratrichlorobenzene: $C_6H_3Cl_3$ (1-3-5), crystals, f. p. 63.4° , b. p. 208° .

Metatetrachlorobenzene: $C_6H_2Cl_4$ (1-2-3-5), crystals, f. p. 50° , b. p. 246° .

Paratetrachlorobenzene: $C_6H_2Cl_4$ (1-2-4-5), crystals, f. p. 137° , b. p. 245° .

Benzyl chloride— $C_6H_5CH_2Cl$ —is an example of the substitution of a halogen in the lateral chain of a superior homologue of benzene. It is obtained by the action of chlorine upon boiling toluene; or of PCl_5 on benzylic alcohol. It is a colorless liquid, boils at 176° , and gives off pungent vapors which excite the lachrymal secretion. It is readily oxidized to benzoic aldehyde or benzoic acid, and serves for the introduction of the radical benzyl into other molecules. The radical of benzylic alcohol ($C_6H_5.CH_2$) is called **benzyl**; that of benzoic acid, ($C_6H_5.CO$), **benzoyl**. The groups C_6H_5 , called **phenyl**, and C_6H_4 , called **phenylene**, behave as radicals, corresponding to the alkyls and alkylenes respectively.

BENZENIC OXYGEN COMPOUNDS.

The derivatives of benzene containing oxygen include, besides alcohols, aldehydes, ketones, acids, ethers, and anhydrides, corresponding to those of the open chain series, a class of hydroxides, the **phenols**, of which there are no aliphatic prototypes.

PHENOLS.

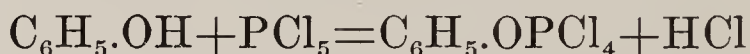
In the phenols the hydroxyl is substituted for the hydrogen of the benzene ring, while in the alcohols the substitution occurs in a lateral chain. Thus phenol is $C_6H_5.OH$; benzylic alcohol, $C_6H_5.CH_2OH$. All six of the hydrogen atoms of benzene may be thus replaced to form **monohydric phenols**, **dihydric phenols**, etc.

In their properties the *phenols differ from the alcohols* by more nearly approaching the character of the acids. On oxidation they do not furnish aldehydes or acids; they do not divide into water and hydrocarbon under the influence of dehydrating agents; they do not react with acids to form esters; they combine directly with Cl and Br to form products of substitution; they form with the metallic elements compounds more stable than similar compounds of the true alcohols.

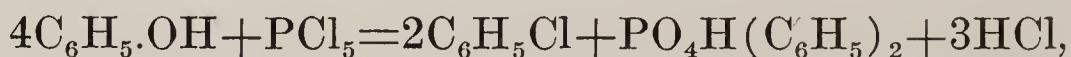
The tertiary aliphatic alcohols are those which most closely resemble the phenols. They both contain the group $C.OH$, triply linked to other carbon atoms: $(H_3C)_2 \backslash C.OH$, and $\begin{smallmatrix} H_3C \\ \backslash \\ C.OH \end{smallmatrix}$, and they also resemble each other in that each is only slowly and imperfectly esterified when heated to 150° with acetic acid. But, while the tertiary alcohols are readily attacked by phosphorus pentachloride, with formation of alkyl chlorides:



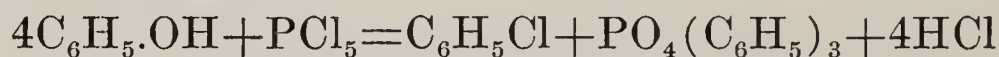
that reagent displaces the hydroxyl of the phenols only imperfectly, or not at all. The products of the reaction with phenol are either phenyl phosphoric tetrachloride:



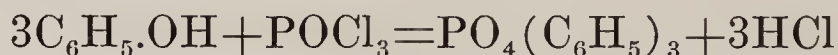
or a mixture of monochlorobenzene with either diphenyl phosphoric acid:



or triphenyl phosphate:



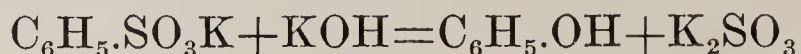
The latter alone is produced by the action of phosphorus oxychloride on phenol:



The phenols occur in nature in small quantities only; some in the vegetable world, and some in combination as ester sulphuric acid in the urine. They are mostly products of distillation of wood, coal, etc.

MONOATOMIC—MONOHYDRIC PHENOLS.

The monoatomic phenols are produced: (1) by fusing the corresponding sulphonic acids with caustic alkali:



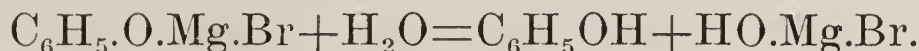
(2) By decomposition of the diazo-compounds by boiling with water:



(3) The higher phenols are produced by heating phenol with ZnCl_2 and the alcohols, a phenolic ether being also formed. Thus phenol and methylic alcohol yield cresol and methyl-phenyl ether:



(4) The phenyl magnesium halides are oxidized by passing air through their ethereal solutions with the formation of compounds of this type: R.O.Mg.X , which when hydrolyzed yield phenols:



The phenols are reduced to hydrocarbons by heating with zinc dust. Their ring-hydrogen is readily replaceable by other elements or groups to form haloid, nitro, amido derivatives, etc. Their hydroxyl hydrogen is also readily replaceable by alkyls to produce ethers, by Na, K, and Ca to produce phenates, and by acidyls to produce phenyl esters. The phenols combine with the diazo-compounds to produce azo- and diazo dyes, and with phthalic acid to produce phthaleïns.

Phenol—Benzophenol—Phenyl hydroxide—Phenic acid—Carbolic acid— $\text{C}_6\text{H}_5.\text{OH}$ —exists in considerable quantity in coal- and wood-tar, and in small quantity in castoreum and, in combination, in the urine. It is produced in the intestine.

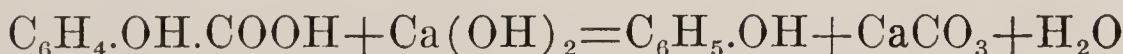
It is formed: (1) by fusing sodium-phenyl sulphide with excess of alkali:



(2) By heating phenyl iodide and potassium hydroxide at 320° :



(3) By heating together salicylic acid and quicklime:



(4) By total synthesis from acetylene, through benzene, and its sulphonic acid.

(5) By decomposition of the phenylic esters by alkalies. Thus salol yields phenol and salicylic acid:



(6) By dry distillation of benzoin.

“Synthetic phenol,” prepared by method (4), is now manufactured. “Carbolic acid” is obtained from the “middle oil” of gas tar (p. 341). It is purified by conversion into potassium phenate, $\text{C}_6\text{H}_5.\text{OK}$, which is crystallized, decomposed by HCl , and the liberated phenol recrystallized and distilled.

Phenol is extensively used, not only as an antiseptic, but also in the manufacture of numerous derivatives, including medicinal compounds, dyes and explosives.

Phenol crystallizes in long, colorless needles, fuses at 43° , boils at 183° , sp. gr. 1.084 at 0° , has a characteristic odor, and an acrid, burning taste, soluble in 15 parts of water at 20° , very soluble in alcohol and in ether, neutral in reaction. It may be distilled without decomposition.

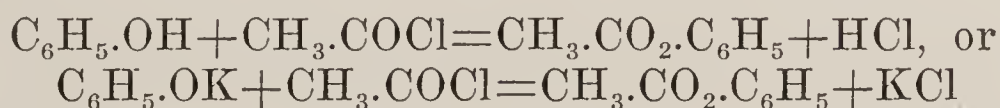
Its vapor is reduced to benzene by heating with Zn. It combines with H_2SO_4 to form o-, and p-phenol sulphonic acids. With HNO_3 it forms 2-4-6-trinitrophenol. Heated with sulphuric and oxalic or arsenic acid, it yields several triphenyl-methane dyes, among which are corallin, rosolic acid, peonin, azulin, aurin, and phenicin.

Analytical Characters—(1) Its peculiar odor. (2) Mix with one quarter volume of NH_4OH ; add two drops of sodium hypochlorite solution, and warm: a blue or green color. Add HCl to acid reaction: turns red. (3) Add two drops of the liquid to a little HCl , and then a drop of HNO_3 : a purple red color. (4) Boil with HNO_3 so long as red fumes are given off; neutralize with KOH : a yellow, crystalline precipitate. (5) Heat with Millon's reagent: a yellow ppt., forming a red solution in HNO_3 . (6) With solution of FeSO_4 : a lilac color. (7) Add excess of bromine water: a yellowish-white precipitate. This compound, tribromophenol, $\text{C}_6\text{H}_2\text{Br}_3\text{OH}$, is the form in which phenol is quantitatively determined; 100 parts of it correspond to 29.8 parts of phenol. (8) Moisten a pine shaving with the liquid, then with HCl , to which a trace of KClO_3 has been added immediately before use, and expose to sunlight: a fine blue color. The test should be tried also with a solution of phenol, and with the acid alone, as only certain varieties of pine are suitable.

Toxicology.—Carbolic acid is an active poison and corrosive. It has caused death in a dose of 1.5 gram. The average duration of fatal cases is 2–8 hours. Death may occur in 3–5 minutes from collapse. It causes a burning sensation, soon followed by intense pain and cauterization of all parts with which it comes in contact. The stain which it produces is at first white, after a few minutes; later it turns darker and, when the eschar separates, a brown stain remains, which persists for many days. Vomiting usually occurs, the vomited matters, as well as the breath, having the odor of carbolic acid. The patient soon becomes unconscious, and death is from collapse or in coma. The urine, normal in color when first voided, soon becomes olive-green, brown, or even black in color. The treatment consists in administration of albumin, saccharated lime, sodium sulphate, or strong alcohol, followed by lavage.

Phenates.—*Carbolates*.—The hydroxyl hydrogen of phenol is replaceable by certain metals and by alkyls to form phenates and phenyl ethers. When phenol and KOH are heated together, **potassium phenate**, $\text{C}_6\text{H}_5\text{OK}$, is formed. This, when treated in alcoholic solution with HgCl_2 , produces **mercuric phenate**, $(\text{C}_6\text{H}_5\text{O})_2\text{Hg}$, a yellow, crystalline solid which has been used in medicine.

Phenol Esters.—The H of the OH of phenol is replaceable by either alkyls or acidyls. With the former phenol plays the part of an acid, and therefore the resulting compounds are the phenol esters, corresponding to the metallic phenates. But, although phenol is not an alcohol, the radical phenyl (C_6H_5)' of which it is the hydroxide, is in all respects equivalent to the alkyls, of which the monohydric alcohols are the hydroxides. Therefore the phenol esters, such as $C_6H_5 \cdot O \cdot CH_3$, are also the phenyl ethers (p. 360). The phenyl esters, on the other hand, may be considered as derivable from phenol by substitution of acidyls for hydroxyl hydrogen: $C_6H_5 \cdot O \cdot (OC \cdot CH_3)$, or as derivable from the acids by substitution of phenyl for carboxyl hydrogen: $CH_3 \cdot COO(C_6H_5)$. The phenyl esters are formed by the action of the acidyl chlorides upon the phenols, or upon their metallic derivatives:



as the aliphatic esters are formed by the action of acidyl halides upon the alcohols or upon the alcoholates.

Cresols—Cresylols—Cresylic acids—Benzylic or cresylic phenols— $C_6H_4 \begin{smallmatrix} \diagup CH_3 \\ \diagdown OH \end{smallmatrix}$ —108.—Of the three possible compounds, two, the para and ortho, accompany phenol in coal-tar, from which they may be separated by fractional distillation. They are more readily obtained pure from toluene. **Creolin**—an antiseptic less poisonous than phenol, consists chiefly of cresols. **Lysol** is impure paracresol, mixed with fat and saponified.

Creosote—Creosotum (U. S. P.)—is a complex mixture containing phenol, cresol, **creasol**, $C_8H_{10}O_2$, **guaiacol**, $C_7H_8O_2$ (see pyrocatechol), and other substances, obtained from wood-tar, and formerly extensively used as an antiseptic. It is an oily liquid, colorless when freshly prepared, but becoming brownish on exposure to light. It has a burning taste and a strong, peculiar odor. It boils at 203° , and does not solidify at -27° .

Xenols—Xylenols.—Theoretically there are six possible xenols which are **dimethyl phenols**, $C_6H_3(CH_3)_2OH$; two derivable from orthoxylylene, three from metaxylylene and one from paraxylylene. They have all been produced synthetically. There are also three possible xenols which are **ethyl phenols**, $C_6H_4(C_2H_5)OH$.

Thymol—3-Methyl-6-isopropyl phenol—Cymylic phenol— $C_6H_3(OH)_{(1)}(CH_3)_{(3)}(C_3H_7)_{(6)}$,—exists, accompanying cymene and thymene, $C_{10}H_{16}$, in essence of thyme, from which it is obtained. It is also prepared synthetically from cuminic aldehyde, $C_6H_4(CHO)_{(1)}(C_3H_7)_{(4)}$.

It crystallizes in large, transparent, rhombohedral tables; has a peppery taste, and an agreeable, aromatic odor. It fuses at 44° , and boils at 230° ; is sparingly soluble in water, very soluble in alcohol and ether. With the alkalis it forms definite compounds, which are very soluble in water. Its reactions are very similar to those of phenol.

Thymol is an excellent deodorizing and antiseptic agent, possessing the advantage over phenol of having itself a pleasant odor.

Aristol is diiodo-thymol, a dibenzenic compound, produced by the action of a solution of I in KI upon an aqueous solution of thymol in the presence of KOH. It is an inodorous, yellowish-red powder, insoluble in H_2O , very sparingly soluble in alcohol, readily soluble in ether and in chloroform. It is decomposed by heat and by light and is said to be a non-poisonous antiseptic.

Carvacrol—2-Methyl-5-isopropyl phenol— $C_6H_3(OH)_{(1)}(CH_3)_{(2)}(C_3H_7)_{(5)}$ —an isomere of thymol, exists in many essential oils, and is obtained by the action of iodine upon camphor; by the action of potash in fusion upon cymene sulphonic acid, $C_{10}H_{13}SO_3H$; or by a transposition of the atoms of another isomere, **carvol**, which exists in caraway oil. It is an oil, boiling at 233° – 235° . Heated with P_2O_5 , it yields orthocresol.

SUBSTITUTED PHENOLS.

Phenol is a monosubstituted derivative, and hence still contains five H atoms which may be replaced by other elements or radicals, to produce di- or tri- or poly-substituted derivatives of benzene, which will be ortho, meta or para, etc., according to the relations of the introduced groups to the OH, already existing in phenol, or to the C_nH_{2n+1} and OH groups in its superior homologues.

Chlorophenols.—The three monochlorinated compounds are obtainable from the corresponding chloranilines. **Orthochlorophenol** (1—2) is a colorless liquid, boils at 175° – 176° , converted into pyrocatechol by KOH. **Metachlorophenol** (1—3) is a liquid, boiling at 214° . KOH converts it into resorcinol. **Parachlorophenol** (1—4) is a crystalline solid, fusible at 37° , converted into quinol by fusion with KOH. Di-, tri-, and penta-chlorophenols are also known.

Bromophenols correspond in method of formation and properties with the Cl derivatives. **2-4-6 Tribromophenol**— $C_6H_2.OH.Br_3$ —is the precipitate formed on adding bromine water to phenol solution. It forms white crystals, fusing at 92° , insoluble in water, soluble in alcohol and ether. It has been used as an antiseptic in diphtheria under the name **Bromol**.

Iodophenols are formed by the action of iodine and K_2S upon phenol in the presence of excess of alkali, or from the corresponding amidophenols. Like the chlorine and bromine derivatives, they yield the corresponding diphenol by the action of KOH in fusion. A tri-iodophenol, formed by the action of solution of I in K_2S upon an alkaline solution of phenol, has been proposed as a substitute for iodoform under the name **annidalin**.

For nitro- and amido-phenols, see pp. 369, 373.

DIATOMIC, OR DIHYDRIC PHENOLS.

Diatomic phenols are derived from the benzenic hydrocarbons by the substitution of two (OH) groups for two atoms of hydrogen. In obedience to the laws of substitution already discussed, three such compounds exist, corresponding to each hydrocarbon.

Pyrocatechol—*Pyrocatechin*—*Oxyphenic acid*—*Orthodioxy-benzene*— $\text{C}_6\text{H}_4(\text{OH})_2$ (1-2) is obtained from catechin or from morintannic acid by dry distillation; also by the action of KOH on orthochlor- or orthiodo-phenol, or by decomposing its methyl ether, **guaiacol**, by HI at 200° . It crystallizes in short, square prisms; fuses at 104° , and boils at 245.5° . Readily soluble in water, alcohol, and ether. Its aqueous solution gives a dark green color with FeCl_3 solution, changing to violet on addition of NH_4OH , NaHCO_3 , or tartaric acid. Its acid sulphuric ester exists in the urine.

M o n o m e t h y l-pyrocatechuic Ether — **Guaiacol** — $\text{C}_6\text{H}_4.\text{OH}(\text{OCH}_3)_{(2)}$ —exists in beech-wood tar, from which an impure (60–90%) guaiacol is obtained as a yellowish liquid, sp. gr. 1.133, boiling at 206° – 207° , by distillation. Pure guaiacol is obtained from this by crystallization at low temperature; by heating pyrocatechol with potassium-methyl sulphate and KOH; also from vanillin, and from veratrol. It is a crystalline solid, fuses at 33° , boils at 205° , soluble in 50 parts of water. Guaiacol has been used in the treatment of phthisis both on account of its germicidal action, and upon the theory that it forms compounds with the toxalbumins, which are readily eliminated. It is also used in numerous forms of combination: in its carbonic esters, as **styracol**=cinnamyl-guaiacol, as **benzosol**=benzoyl-guaiacol, as **thiocol**=guaiacol-potassium sulphonate, and in combination with salicylic acid.

Dimethyl-pyrocatechuic Ether—**Veratrol**— $\text{C}_6\text{H}_4(\text{OCH}_3)_{2(1-2)}$ —is an oil, crystallizing at 15° , formed by distilling veratric acid, or by acting upon the potassium salt of guaiacol with methyl iodide.

Resorcinol—*Resorcin*—*Metadioxy-benzene*— $\text{C}_6\text{H}_4(\text{OH})_{2(1,2)}$, is obtained by the action of fused KOH on metachlor-, or iodophenol. It is also prepared by dry distillation of extract of Brazil wood.

It forms short, thick, colorless and odorless, rhombic prisms. Fuses at 104° , and boils at 271° . It is very soluble in water, alcohol, and ether. Its aqueous solution is neutral in reaction, and intensely sweet. With FeCl_3 its solutions assume a dark-violet color, which is discharged by NH_4OH . Its ammoniacal solution by exposure to air, assumes a pink color, changing to brown and, on evaporation, green and dark blue. Heated with phthalic anhydride at 195° it yields **fluoresceine**. It dissolves in fuming H_2SO_4 , forming an orange-red solution, which becomes darker, changes to greenish-black, then to pure blue, and finally to purple on being warmed.

Resorcinol, heated with sodium nitrite and H_2O to about 150° yields a blue pigment known as **lacmoid**, which behaves like litmus with acids and alkalies, but is more sensitive.

Quinol — *Hydroquinone* — *Paradioxy-benzene*— $\text{C}_6\text{H}_4(\text{OH})_{2(1,4)}$ is formed by fusing paraiodo-phenol with KOH at 180° , by dry distillation of oxysalicylic acid or of quinic acid, and by the action of reducing agents on quinone. It forms colorless, rhombic prisms,

which fuse at 169° . Readily soluble in water, alcohol, or ether. Its aqueous solution is turned red-brown by NH_4OH . Oxidizing agents convert it into quinone.

TRIATOMIC, OR TRIHYDRIC PHENOLS.

Phloroglucin— $\text{C}_6\text{H}_3(\text{OH})_3$ (1, 3, 5)—is obtained by the action of potash upon phloretin, quercitrin, maclurin, catechin, kino, etc. It crystallizes in rhombic prisms, containing 2Aq; is very sweet; and very soluble in water, alcohol, and ether.

Pyrogallol—*Pyrogallic acid*— $\text{C}_6\text{H}_3(\text{OH})_3$ (1, 2, 3)—is formed when gallic acid is heated to 200° . It crystallizes in white needles; neutral in reaction; very soluble in water; very bitter; fuses at 132° ; boils at 210° ; poisonous. Its most valuable property is that of absorbing oxygen, for which purpose it is used in the laboratory in the form of a solution of potassium pyrogallate.

PHENOL DYES.

Aurin— $\text{C}_{19}\text{H}_{14}\text{O}_3$, and **Rosolic acid**— $\text{C}_{20}\text{H}_{16}\text{O}_3$ —are substances existing in the dye obtained by the action of oxalic acid upon phenol in presence of H_2SO_4 , known as **corallin**, or **pæonin**, which communicates to silk or wool a fine yellow-red color.

Aurin crystallizes in fine, red needles from its solution in HCl . It is insoluble in H_2O , but soluble in HCl , alcohol, and glacial acetic acid. It forms a colorless compound with potassium bisulphite.

Phthaleïns.—These substances are produced by heating the phenols with phthalic anhydride, $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$, water being at the same time eliminated.

Their constitution is that of a benzene nucleus, two of whose H atoms have been replaced by two acetone groups (CO), whose remaining valences attach them to two phenol groups by exchange with an atom of hydrogen.

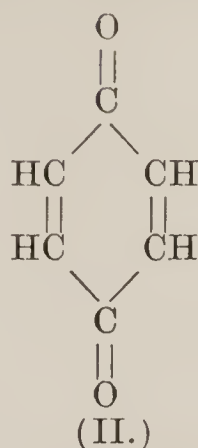
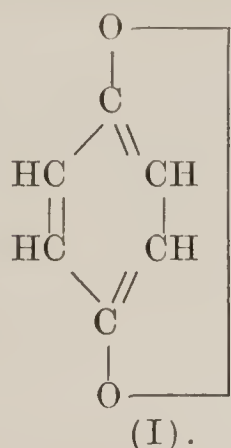
Thus **phenol-phthaleïn**, the simplest of the group, has the constitution, $\text{C}_6\text{H}_4 \begin{matrix} \diagup \text{CO} - \text{C}_6\text{H}_4(\text{OH}) \\ \diagdown \text{CO} - \text{C}_6\text{H}_4(\text{OH}) \end{matrix}$. Phenol-phthaleïn is a yellow, crystal powder, insoluble in water, but soluble in alcohol. Its alcoholic solution, perfectly colorless if neutral, assumes a brilliant magenta-red in the presence of an alkali. This property renders phenol-phthaleïn very valuable as an *indicator* of reaction.

Resorcinol-phthaleïn—**Fluoresceïne**— $\text{C}_{20}\text{H}_{12}\text{O}_5$ —bears the same relation to resorcinol that phenol-phthaleïn does to phenol, and is obtained from resorcinol by a corresponding method. It is a dark-brown crystalline powder, which dissolves in ammonia to form a red solution, exhibiting a most brilliant green fluorescence. A tetra-bromo-derivative of fluoresceïne is used as a dye under the name **eosin**.

QUINONES.

The quinones are benzene derivatives in which two atoms of hydrogen are replaced by two oxygen atoms. The attachment of the $-\text{O.O}-$ group is either ortho- or para-, never meta-. **Ortho-quinones** of the polybenzenic series, such as β naphthoquinone and anthroquinone, are well-known compounds, but the mono-benzenic ortho-quinones are only known in their derivatives.

The monobenzenic para-quinones may be considered either as peroxides, the bonds of the benzene ring remaining intact (Formula I), or they may be considered as



ring-ketones (Formula II), in which the two CO groups form a part of an oxidized hydroaromatic ring. The former view is favored by the facts that the quinones are strong oxidizing agents, as are the peroxides in general, and that they yield monosubstituted derivatives

by replacement of their oxygen by univalents, as benzoquinone forms p-dioxybenzene, $(\text{HO})\text{C} \begin{smallmatrix} \diagup \text{CH}:\text{CH} \diagdown \\ \diagdown \text{CH}.\text{CH} \diagup \end{smallmatrix} \text{C}(\text{OH})$ on reduction, and p-dichlorobenzene, $\text{ClC} \begin{smallmatrix} \diagup \text{CH}:\text{CH} \diagdown \\ \diagdown \text{CH}.\text{CH} \diagup \end{smallmatrix} \text{CCl}$, by the action of PCl_5 . On the other hand, the existence of the $\text{CO}=\text{group}$ in the quinones is indicated by the fact that they readily form oximes with hydroxylamine, a reaction characteristic of compounds containing $\text{CO}=\text{}$, as benzoquinone forms quinone dioxime, $\text{HO.NC} \begin{smallmatrix} \diagup \text{CH}:\text{CH} \diagdown \\ \diagdown \text{CH}.\text{CH} \diagup \end{smallmatrix} \text{CN.OH}$; and if, by reason of its oxidation of phenylhydrazine, benzoquinone forms no phenylhydrazone such compounds are formed by the naphthoquinones.

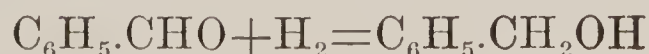
Quinone—Benzoquinone— C_6H_4 : $\begin{smallmatrix} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{smallmatrix}$ —is formed by the action of oxidants upon a variety of p-benzene derivatives, but best by limited oxidation of quinic acid. It crystallizes in golden-yellow prisms, f. p. 116° , sublimates at ordinary temperatures, sparingly soluble in cold water, readily soluble in hot water, alcohol and ether. It has a peculiar, pungent odor, stimulates the lachrymal secretion, and irritates the skin. Reducing agents convert it into quinol.

AROMATIC ALCOHOLS.

The alcohols corresponding to this series of hydrocarbons are isomeric with the phenols. They contain the characterizing group of the primary alcohols, CH_2OH ; once if the alcohol be monoatomic, twice if diatomic, etc., and they yield on oxidation, first an aldehyde and then an acid. Thus: $\text{C}_6\text{H}_5.\text{CH}_2\text{OH}$ =benzylic alcohol; $\text{C}_6\text{H}_5.\text{CHO}$ =benzoic aldehyde; $\text{C}_6\text{H}_5.\text{COOH}$ =benzoic acid.

The monohydric aromatic alcohols are produced by reactions similar to those by which the corresponding aliphatic compounds are produced (p. 212):

(1) By reduction of the corresponding aldehydes:



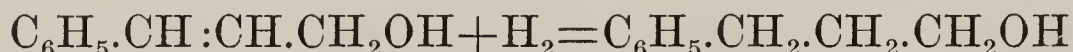
(2) By saponification of alkyl benzenes having a halogen atom in a lateral chain:



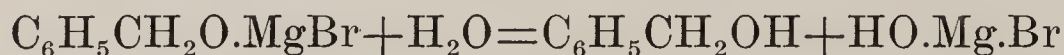
(3) By the action of nitrous acid on the primary amides having the amido group in a lateral chain:



(4) By reduction of the unsaturated alcohols such as cinnamic alcohol:



(5) By the action of trioxymethylene upon phenyl magnesium halides:



They are capable of yielding isomeric products of further substitution, ortho, para, or meta.

Benzylic Alcohol—Benzoic Alcohol—Benzyl Hydrate— $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{OH}$ —does not exist in nature, and is of interest chiefly as corresponding to two important compounds, benzoic acid and benzoic aldehyde (oil of bitter almonds). It is obtained by the action of potassium hydroxide upon oil of bitter almonds, or by slowly adding sodium amalgam to a boiling solution of benzoic acid.

It is a colorless liquid; boils at 206.5° ; has an aromatic odor; is insoluble in water, soluble in all proportions in alcohol, ether, and carbon bisulphide. By oxidation it yields, first, benzoic aldehyde, $\text{C}_6\text{H}_5\text{CHO}$; and afterward, benzoic acid, $\text{C}_6\text{H}_5\cdot\text{COOH}$. By the same means it may be made to yield products similar to those obtained from the alcohols of the saturated hydrocarbons.

Secondary and tertiary aromatic alcohols are also known, such as **phenyl-methyl carbinol**, $\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{CH}_3$ and **phenyl-dimethyl carbinol**, $\text{C}_6\text{H}_5\cdot\text{COH}(\text{CH}_3)_2$. The secondary alcohols yield ketones on oxidation (p. 354).

Di- and tri-hydric alcohols, such as the **xylylene glycols**, $\text{C}_6\text{H}_4(\text{CH}_2\text{OH})_2$, and **mesitylene glycerol**, $\text{C}_6\text{H}_3(\text{CH}_2\text{OH})_3$ (1-3-5), are also known, as well as alcohols with unsaturated lateral chains, such as **cinnamic alcohols**, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{OH}$, which occurs as its cinnamic ester in *storax*. It oxidizes to cinnamic aldehyde and cinnamic acid.

ALPHENOLS, OR OXYPHENYL ALCOHOLS.

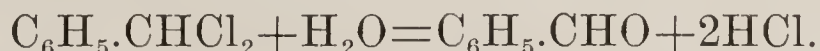
These substances are intermediate in function between the alcohols and the phenols, and contain both substituted groups OH and CH_2OH .

Saligenin—*o*-Oxybenzylic Alcohol— $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}_2\text{OH} \\ \diagdown \text{OH} \end{smallmatrix}$ —is obtained from salicin in large, tabular crystals; quite soluble in alcohol, water, and ether. Oxidizing agents convert it into salicylic aldehyde, which by further oxidation yields salicylic acid. It is also formed by the action of nascent hydrogen on salicylic aldehyde.

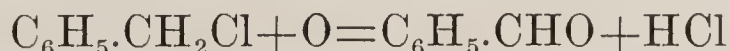
ALDEHYDES.

The aromatic aldehydes are the first products of oxidation of the aromatic alcohols. **Monaldehydes** containing one CHO group and **dialdehydes** containing two such groups are known.

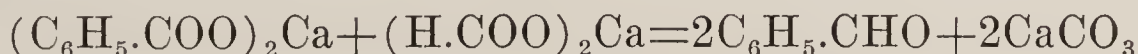
The monaldehydes are formed: (1) By oxidation of the alcohols; (2) By decomposition of the alcohol bichlorides by water:



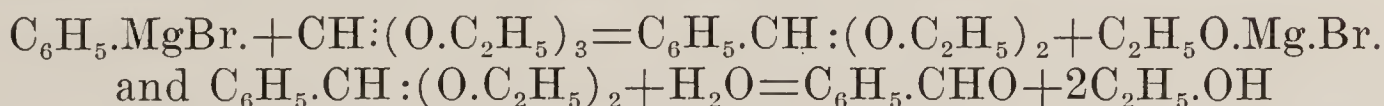
(3) By oxidation of the alcohol monochlorides by lead nitrate:



(4) By distilling a mixture of the Ca salt of the acid and calcium formate:



(5) By prolonged boiling of phenyl magnesium halides with orthoformic esters, and hydrolysis of the product:



(6) By the action of chromyl chloride, CrO_2Cl_2 , upon the hydrocarbons, and decomposition of the addition compound by water.

Benzoic Aldehyde—Benzoyl hydride— $\text{C}_6\text{H}_5.\text{CHO}$ —is the main constituent of oil of bitter almonds, although it does not exist in the almond. It is formed, along with hydrocyanic acid and glucose, by the action of water upon amygdalin. It is also formed by the general methods given above; by the dehydration of benzylic alcohol; by the dry distillation of a mixture in molecular proportions of calcium benzoate and formate; by the action of nascent hydrogen upon benzoyl cyanide, etc. It is obtained from bitter almonds. The crude oil contains, besides benzoic aldehyde, hydrocyanic and benzoic acids and benzoyl cyanide.

It is a colorless oil, having an acrid taste and the odor of bitter almonds; sp. gr. 1.050; boils at 179.4° ; soluble in 30 parts of water, and in all proportions in alcohol and ether. Oxidizing agents convert it into benzoic acid, a change which occurs by mere exposure to air. Nascent hydrogen converts it into benzylic alcohol. With Cl and Br it forms benzoyl chloride or bromide: H_2SO_4 dissolves it when heated, forming a purple-red color, which turns black if more strongly heated. It forms a series of products of substitution, haloid, nitro, amido, etc.

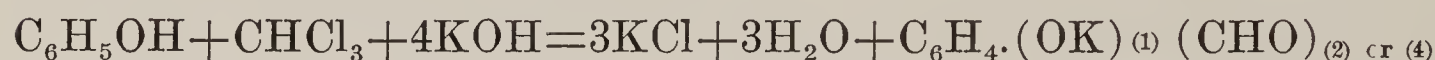
When perfectly pure, benzoic aldehyde exerts no deleterious action when taken internally; owing, however, to the difficulty of completely removing the hydrocyanic acid, the substances usually sold as *oil of bitter almonds*, *ratafia*, and *almond flavor*, are almost always poisonous, if taken in sufficient quantity. They may contain as

much as 10–15 per cent. of hydrocyanic acid, although said to be “purified.” The presence of the poisonous substances may be detected by the tests given on page 304.

Salicylic Aldehyde—*Salicyl hydride*—*Salicylal*—*Salicylous acid*—*o-Oxybenzaldehyde*— $C_6H_4(OH)(CHO)_{(2)}$ —exists in the flowers of *Spiræa ulmaria*, and is the principal ingredient of the essential oil of that plant. It is best obtained by oxidizing salicin.

It is a colorless oil; turns red on exposure to air; has an agreeable, aromatic odor, and a sharp, burning taste; sp. gr. 1.173 at 13.5; boils at 196.5°; soluble in water, more so in alcohol and in ether.

It is, as we should suspect from its origin, a substance of mixed function, possessing the characteristic properties of aldehyde and phenol, an oxymonaldehyde, or phenol aldehyde. Compounds of this class are formed by the action of chloroform upon the phenols in the presence of a caustic alkali, when the CHO enters the ortho- or para-position with reference to the phenolic hydroxyl. Thus phenol yields ortho- or para-salicylic aldehyde:

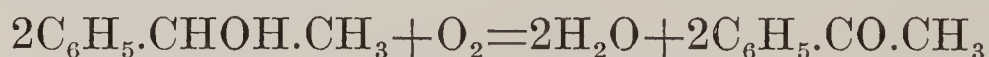


It produces a great number of derivatives, some of which are salts or esters, such as **p-methoxybenzaldehyde**, or **anisic aldehyde**, $C_6H_4(CHO)(OCH_3)_{(4)}$, a product of oxidation of **anethol**.

Vanillin—**Methylprotocatechuic Aldehyde**—**m-Methoxy-p-oxybenzaldehyde**— $C_6H_3.CHO.(O.CH_3)_{(3)}(OH)_{(4)}$ —a methylated dioxybenzaldehyde, is the odoriferous principle of vanilla. It is produced artificially by oxidation of **coniferin**, $C_{16}H_{22}O_8$, a glucoside occurring in coniferous plants. It crystallizes in needles, fuses at 80°, is sparingly soluble in water, readily soluble in alcohol or ether. It has a pungent taste and a persistent odor of vanilla. On exposure to air it becomes partly oxidized to **vanillic acid**, $C_8H_8O_4$.

KETONES.

The aromatic ketones are produced by the oxidation of the secondary aromatic alcohols:



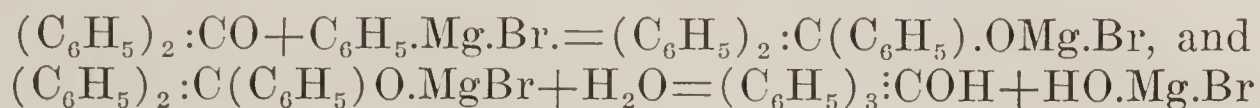
Or by the action of caustic potash upon the aromatic β ketone-carboxylic acids:



Monoketones, **diketones** and **triketones**, containing one, two and three lateral chains with CO groups, are known. The **monoketones**, also called **phenones**, consist of a closed chain hydrocarbon group united to an open chain one by the group (CO)". They may also be considered as benzene, into which fatty acid radicals have been substituted for hydrogen.

The phenones containing two aromatic nuclei, as benzophenone: $C_6H_5.CO.C_6H_5$, belong to the diphenyl derivatives.

The phenones are acted upon by the alkyl magnesium halides in the same manner as are those of the aliphatic series (p. 226). Thus benzophenone and phenyl magnesium bromide produce triphenyl carbinol:



Phenyl-methyl Ketone—Acetyl benzene—Acetophenone—Hypnone— $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_3$ —is obtained by distilling a mixture of calcium benzoate and acetate; by the action of zinc-methyl upon benzoyl chloride; or by the action of acetyl chloride or bromide upon benzene in the presence of aluminium chloride. It forms large crystalline plates, fusible at 20° . It has been used as a hypnotic.

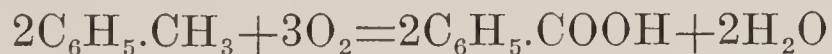
Acetophenone Oxime— $\text{C}_6\text{H}_5.\text{C}:(\text{N}.\text{OH}).\text{CH}_3$ —is isomeric with acetanilide, $\text{C}_6\text{H}_5\text{NH}(\text{CO}.\text{CH}_3)$, and is converted into that substance by the action of concentrated H_2SO_4 .

AROMATIC CARBOXYLIC ACIDS.

All six of the hydrogen atoms of benzene are replaceable by carboxyl groups, with formation of monocarboxylic acids, dicarboxylic acids, etc. There are also three series, o-, m-, and p-, of the bi-, tri-, and tetracarboxylic acids, and of the monocarboxylic acids above the first. These acids may be obtained by oxidation of the corresponding alcohols, or aldehydes, where these are known. Like the aliphatic acids, they may be considered as being derived from the hydrocarbons by substitution of hydroxyl and oxygen for hydrogen in a lateral chain.

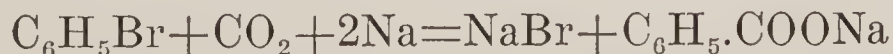
MONOCARBOXYLIC AROMATIC ACIDS—BENZOIC SERIES.

These acids are formed by many methods, among which the most important are: (1) By oxidation of the lateral chain in hydrocarbons homologous with benzene. Thus toluene yields benzoic acid:

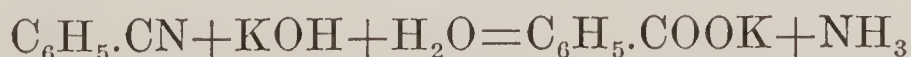


(2) By oxidation of the corresponding alcohols and aldehydes.

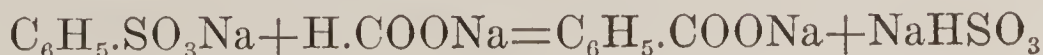
(3) By the action of sodium and carbon dioxide upon the monobromobenzenes:



(4) By decomposition of the aromatic acid nitriles by acids or alkalies:



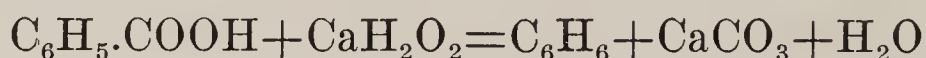
(5) By fusion of the aromatic sulphonic acids with sodium formate:



The acids of this series form many derivatives. In some of these the carboxyl is modified, leaving either the radical **benzoyl**, $\text{C}_6\text{H}_5\text{.CO}$, as in **benzamide**, $\text{C}_6\text{H}_5\text{.CO.NH}_2$, or the trivalent group **benzenyl**, $\text{C}_6\text{H}_5\text{.C}$, as in **benzenyl-amidine**, $\text{C}_6\text{H}_5\text{.C} \begin{smallmatrix} \diagup \text{NH}_2 \\ \diagdown \text{NH} \end{smallmatrix}$. In others the substitution occurs in the benzene ring, as in the oxy-, halogen-, and nitro-benzoic acids, etc., *e.g.* **anthranilic** or **o-amido-benzoic acid** $\text{C}_6\text{H}_4\text{.COOH}_{(1)}(\text{NH}_2)_{(2)}$.

Benzoic Acid— $\text{C}_6\text{H}_5\text{.COOH}$ —exists in benzoin, tolu balsam, castoreum, and in several resins. It is obtained by the general methods given above; also from benzoin, and from the urine of herbivorous animals. The urine contains hippuric acid, which, on decomposition, yields benzoic acid. Conversely, when benzoic acid is taken into the body in moderate doses it is eliminated as hippuric acid.

Benzoic acid crystallizes in white, transparent plates; the solid acid is odorless, but its vapor has a peculiar odor and produces a tendency to sneeze; it is sparingly soluble in cold water, readily soluble in hot water, in alcohol and in ether; fuses at 120° , boils at 250° , and sublimes at temperatures below its boiling point. Benzoic acid is not attacked by HNO_3 . Heated with lime, it yields benzene and calcium carbonate:



a reaction corresponding to the formation of methane from sodium acetate. The benzoates are all soluble, the least soluble being the ferric salt.

Homologues of Benzoic Acid.—These are of two kinds: (1) Those in which the carboxyl and hydrocarbon groups replace different hydrogen atoms, the **alkyl-benzoic acids**, as **cumic acid**, or **p-isopropyl benzoic acid**, $\text{C}_6\text{H}_4\text{.(C}_3\text{H}_7\text{)}_{(1)}(\text{COOH})_{(4)}$. (2) Those in which the carboxyl is separated from the benzene ring by a hydrocarbon group, the **phenyl fatty acids**, as **phenyl-acetic acid**, $\text{C}_6\text{H}_5\text{.CH}_2\text{.COOH}$. In the terms above the first of this series there are place isomeres according to the distance from the ring in which the carboxyl is introduced. Thus **α phenyl-propionic acid**, $\text{C}_6\text{H}_5\text{.CH} \begin{smallmatrix} \diagup \text{COOH} \\ \diagdown \text{CH}_3 \end{smallmatrix}$ and **β phenyl-propionic acid**, $\text{C}_6\text{H}_5\text{.CH}_2\text{.CH}_2\text{.COOH}$.

POLYCARBOXYLIC AROMATIC ACIDS.

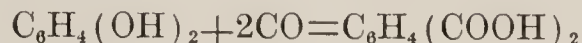
The di-, tri-, tetra-, penta-, and hexa-carboxylic aromatic acids are derived from benzene by substitution of from two to six carboxyls for hydrogen atoms. Of the superior homologues there exist a number of isomeres, increasing with the number of carbon atoms, according as the carboxyls are attached to the benzene ring, as in the phthalic acids, or are contained in lateral chains, as in **phenyl-malonic acid**, $\text{C}_6\text{H}_5\text{.CH(COOH)}_2$, and varying further by differences in orientation either in the benzene or the lateral chains.

Phthalic Acids— $\text{C}_6\text{H}_4(\text{COOH})_2$ —Ortho-, meta-, and para-phthalic acids are produced by oxidation of the corresponding bisubstituted benzene derivatives, and serve by their formation to determine whether a given compound is o-, m-, or p-.

Phthalic Acid—Benzene-o-dicarboxylic acid— $C_6H_4(COOH)_2$ (1, 2) —is obtained: (1) industrially by oxidation of naphthalene or tetra-chloronaphthalene, for use in the manufacture of the phthalein dyes; (2) by oxidation of o-xylene, o-toluic acid, etc.; (3) by direct union of carbon monoxide with salicylic acid:



or with resorcinol:



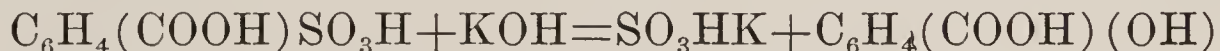
Phthalic acid crystallizes in prisms, sparingly soluble in cold water, readily soluble in hot water, alcohol, and ether, fuses at 213° . Heated with excess of $Ca(OH)_2$, it is decomposed into benzene and CO_2 ; but when its Ca salt is heated to 350° with one molecule of $Ca(OH)_2$ only one CO_2 is expelled, leaving calcium benzoate. Nascent hydrogen converts it into **hydrophthalic acids**. It is the only phthalic acid which yields an anhydride.

Isophthalic Acid—Benzene-m-dicarboxylic acid— $C_6H_4(COOH)_2$ (1, 3) —is formed by oxidation of m-xylene, m-toluic acid, and other m-benzene bisubstituted derivatives. It crystallizes in fine needles, sparingly soluble in water, soluble in alcohol, fuses and sublimes above 300° .

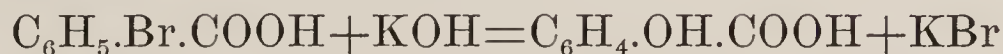
Terephthalic Acid—Benzene-p-dicarboxylic acid— $C_6H_4(COOH)_2$ (1, 4) —is formed by oxidation of p-xylene, p-toluic acid, and other p-benzene bisubstituted derivatives. It is insoluble in water, alcohol, and ether, and sublimes without melting.

PHENOL CARBOXYLIC ACIDS AND THEIR ESTERS.

These compounds have both hydroxyl and carboxyl attached to the benzene ring. They have the functions of phenol and of acid. They are formed (1) by fusing the sulphobenzoic acids with alkalis:



also similarly from the haloid acids:



(2) By fusion of the homologues of phenol with caustic potash, the methyl of the hydrocarbon lateral chain is oxidized to carboxyl.

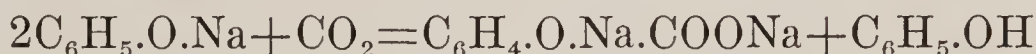
(3) By oxidation of the phenol-aldehydes by fusion with caustic alkalis.

(4) By saponification of their esters, produced by oxidizing the sulphuric or phosphoric esters of the homologues of phenol.

(5) By heating the phenols with carbon tetrachloride and caustic potash:



(6) By the action of carbon dioxide upon the sodium phenates:



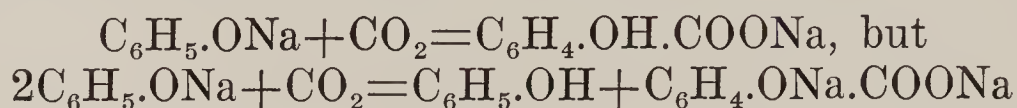
Di-, tri-, and tetra-carboxylic oxyacids are known. But the best known of the oxyacids are monocarboxylic, and monoxy-, dioxy-, and trioxy-, corresponding to the phenols of like hydroxyl content.

MONOXY-MONOCARBOXYLIC ACIDS.

Oxybenzoic Acids— $C_6H_4.OH.CO_2H$.—Of the three isomeric acids the meta-, f. p. 200° , and the para-, f. p. 210° , acids are ob-

tained by the action of KOH on the corresponding bromobenzoic acids.

Salicylic Acid—o-Oxybenzoic Acid—f. p. 155° occurs free, accompanied by salicylic aldehyde, in *Spiræa ulmaria* and, as its methylic ester, in oil of wintergreen. It is also formed by decomposition of salicin, coumarin or indigo. It is produced synthetically by the above reactions and, industrially, by heating sodium phenate in a current of carbon dioxide. The reaction is not

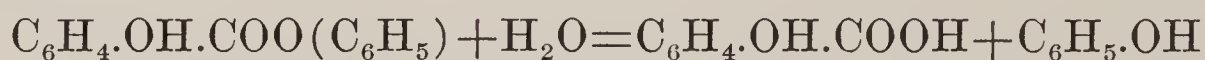


Salicylic acid crystallizes in prisms or needles, sparingly soluble in cold water, readily soluble in hot water, alcohol and ether, sweet and acid in taste. When heated, it distils in part unchanged, while a part loses oxygen and yields salol and **xanthone**, $\text{C}_{13}\text{H}_{10}\text{O}_2$; or salol, carbon dioxide and water. With Cl and Br it forms products of substitution. With fuming HNO_3 it forms a nitro-acid and finally, picric acid. With ferric chloride it gives a fine violet color. Nascent hydrogen causes rupture of the ring, with formation of pimelic acid as a final product. Salicylic acid and its salts and esters are used as antiseptics and as antirheumatics.

Phenyl Salicylate—Salol— $\text{C}_6\text{H}_4.\text{OH}.\text{COO}(\text{C}_6\text{H}_5)$ —is formed by heating salicylic acid to 220° :



also by the action of POCl_3 on a mixture of salicylic acid and phenol. It is a white, crystalline powder, faintly aromatic in taste and odor, almost insoluble in water, soluble in alcohol, ether and benzene, fuses at 43° . It is not decomposed by weak acids, but is saponified by alkalies to form salicylic acid and phenol; hence it passes unchanged through the stomach to be decomposed in the intestine:



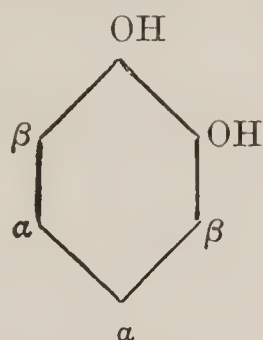
Acetol Salicylate — Salacetol — $\text{C}_6\text{H}_4.\text{OH}.\text{COO}(\text{CH}_2.\text{CO}.\text{CH}_3)$ —the ester of the keto-alcohol, acetol, is formed by the action of monochloroacetone on sodium salicylate. It crystallizes in plates, sparingly soluble in water, readily soluble in alcohol, fusible at 71° . It is saponified by alkalies with formation of acetol and salicylic acid, and is hence substituted for salol as a medicine when the formation of phenol is undesirable. Like acetol and its other esters, it reduces Fehling's solution.

DI- AND TRIOXYMONOCARBOXYLIC ACIDS.

Dioxy-carboxylic Acids.—The six isomeres corresponding to the three diphenols are known, as well as numerous alkyl derivatives, such as vanillic,

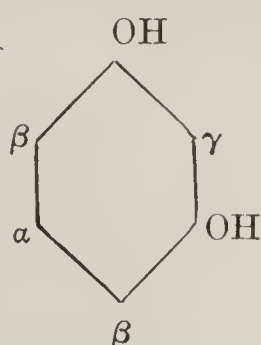
isovanillic and veratric acids, which are derived from protocatechuic acid. The relations of these acids are shown by the following formulæ:

PYROCATECHOL.



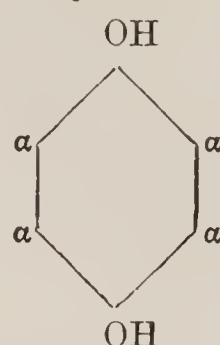
α = 3,4-Dioxybenzoic.
= Protocatechuic.
 β = 2,3-Dioxybenzoic,

RESORCINOL.

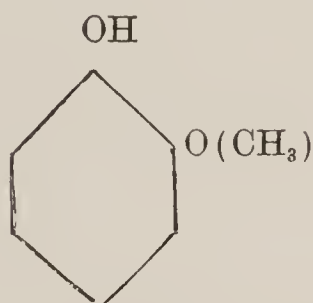


α -Resorcylic,
= 3,5-Dioxybenzoic,
 β -Resorcylic,
= 2,4-Dioxybenzoic.
 γ Resorcylic,
= 2,6-Dioxybenzoic.

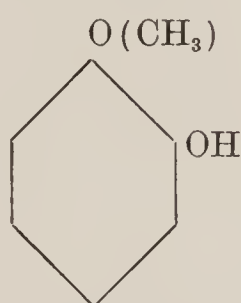
QUINOL.



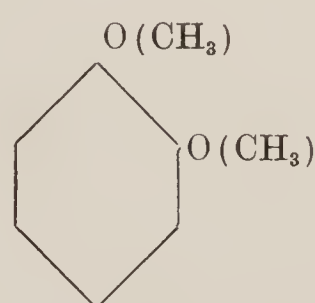
2,5-Dioxybenzoic,
= Gentisinic,
= Hydroquinone-carboxylic.



Vanillic acid.



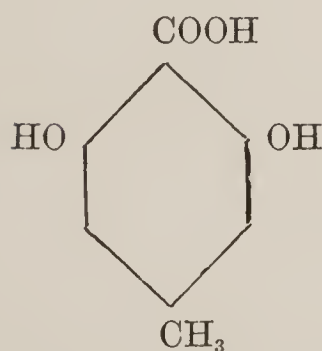
Isovanillic acid.



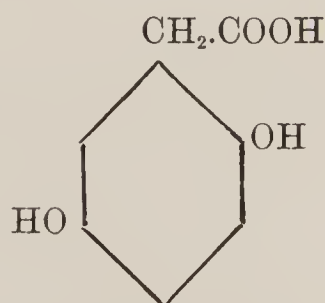
Veratric acid.

Protocatechuic Acid—3,4-Dioxybenzoic Acid— $C_6H_3(COOH)_{(1)}(OH)_{2(3,4)}$ —exists in the fruit of the star-anise, and is produced from many resins by fusion with KOH. It is formed by fusion of dibromobenzoic acid, and other similar derivatives, with KOH.

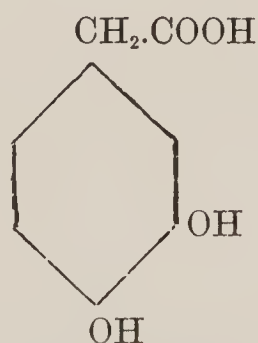
The **superior homologues** of dioxycarboxylic acids are either **dioxytoluic acids**, etc., such as orsellinic acid, or **dioxy-phenyl fatty acids**, such as homogentisinic acid:



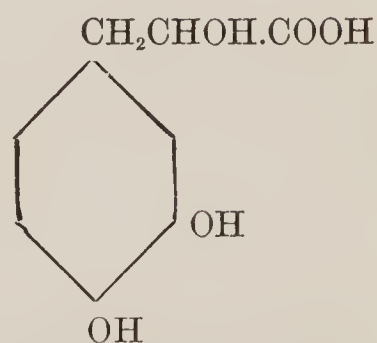
2,6-Dioxyparatoluic.
= Orsellinic.



2,5-Dioxyphenyl-acetic.
= Homogentisinic.



3,4-Dioxyphenyl-acetic.
= Homoprotocatechuic.



3,4-Dioxyphenyl-lactic.
= Uroleucic (?)

Homogentisinic acid, or **glycosuric acid**, exists in the urine in “alkaptonuria,” probably accompanied by **homoprotocatechuic** and **uroleucic** acids, as well as by the monoxy-monocarboxylic acids mentioned above.

Trioxycarboxylic Acids.—Three of the six possible acids are known, two derived from pyrogallol, one from phloroglucin.

Gallic Acid— $C_6H_2(COOH)_{(1)}(OH)_{3(3,4,5)}$ —exists in nature in certain leaves, seeds and fruits. It is best obtained from nut-galls, which contain its glucoside, gallo-tannic acid. It is formed when bromo-protocatechuic acid is fused with

caustic potash. It crystallizes in long, silky needles with 1Aq, odorless, acidulous in taste, sparingly soluble in cold water, very soluble in hot water and in alcohol. Its solutions are acid. When heated to 210–215° it yields CO₂ and pyro-gallol. Its solutions reduce the salts of silver and of gold; they do not precipitate gelatin nor the salts of the alkaloids, as does tannin; and they give a blue-black precipitate with FeCl₃.

Tannins—Tannic Acid—are substances of vegetable origin, principally derived from leaves, barks and seeds. They are amorphous, soluble in water, astringent, capable of precipitating albumin, of forming imputrescible compounds with the gelatinoids (leather), and give green or blue colors with the ferric salts.

Pure tannic acid has been obtained by removal of water from gallic acid: $2C_7H_6O_5 = C_{14}H_{10}O_9 + H_2O$; it is, therefore, **digallic acid**. It exists in gall-nuts, excrescences produced upon oak trees by the punctures of certain insects (gallo-tannic acid). It is colorless, amorphous, odorless, very soluble in water, less so in alcohol, almost insoluble in ether. It forms a dark-blue liquid (ink) with solutions of ferric salts or, after exposure to air, with ferrous salts.

Caffetannic Acid, C₃₀H₁₉O₁₆, exists in saline combination in coffee and Paraguay tea. It colors the ferric salts green, precipitates the salts of quinine and cinchonine, but not tartar emetic or gelatin, as tannic acid does. It yields **caffeic acid**, or **3-4 dioxycinnamic acid**, C₉H₈O₄, on decomposition. **Cachou-tannic acid** obtained from catechu, is soluble in water, alcohol and ether. It precipitates gelatin, but not tartar emetic, and colors ferric salts grayish-green. **Morintannic acid**, or **maclurine**, C₁₃H₁₀O₆, is a yellow, crystalline substance, obtained from fustic. It is more soluble in alcohol than in water. Its solutions precipitate greenish-black with ferric salts, yellow with lead acetate, brown with tartar emetic and yellowish-brown with cupric sulphate. **Quercitannic acid**, C₁₉H₁₆O₁₀, is the tannin of oak bark. It is a red powder, sparingly soluble in water, which forms a violet-red precipitate with ferric salts. **Quinotannic acid** exists in cinchona barks, in combination with the alkaloids. It is light yellow, soluble in water, alcohol and ether, astringent, but not bitter in taste. It is colored green by ferric salts. Dilute H₂SO₄ decomposes it with formation of **quina red**, an amorphous substance, which yields protocatechuic and acetic acids on further decomposition.

PHENYLIC ETHERS—GLUCOSIDES.

The oxides of the aromatic series, corresponding to the aliphatic ethers, and containing two cyclic hydrocarbon groups united by an oxygen atom, properly belong among the dibenzenic compounds, but are more conveniently considered here.

Phenyl Ether—Diphenyl Oxide—(C₆H₅)₂O—is formed by heating phenol with aluminium chloride, or with zinc chloride:



and by other more circuitous methods. It crystallizes in long needles, having the odor of geranium, soluble in alcohol and in ether. Corresponding to it are a number of derivatives, formed by substitution of various univalents for the remaining phenol hydrogen.

The **mixed oxides**, containing a phenyl and an alkyl group, are the phenyl ethers or phenol esters, derived from phenol. They are formed by heating metallic phenates with alkyl halides:



as the aliphatic ethers are produced from metallic alcoholates and alkyl halides.

Methyl-phenyl Ether—Anisol—C₆H₅.O.CH₃—is a colorless, thin liquid,

boils at 152° without decomposition. Sulphuric acid dissolves it, with formation of methyl-phenol sulphonic acid.

Ethyl-phenyl Ether—Phenetol— $C_6H_5.O.C_2H_5$ —is a colorless liquid, having an aromatic odor. It boils at 172°.

GLUCOSIDES.

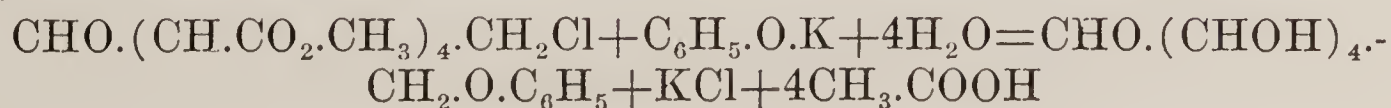
The name “glucoside” was first applied to certain natural products, some of which are the active constituents of medicinal plants, which, on decomposition by dilute mineral acids, yield glucose and some other substance. Subsequently, it was found that the sugars derived from some of these substances differ from glucose; some are pentoses, others hexoses; some monosaccharides, others disaccharides; some aldoses, others ketoses. On the other hand, the second product of decomposition has been of the most varied character, phenols, alphenols, alcohols, oxyphenols, monobenzenic or dibenzenic, but, in all those natural glucosides which have been investigated, always a cyclic compound, containing a phenolic or an alcoholic group. The glucosides have usually been regarded as esters of glucose, etc., since the alcoholic character of the sugars has been recognized, but, as the union of the sugar and benzenic components is through an oxygen atom, and not by replacement of the hydrogen of a carboxyl, they are more properly regarded as ethers, formed by union of an aldose or ketose remainder with one of a phenolic or alcoholic benzenic compound, with elimination of H_2O . The constitution of the glucosides cannot, however, be considered as established, as no natural glucoside has been obtained synthetically, although the products of decomposition of some are comparatively simple compounds. It is to be supposed that the union takes place through the aldehyde group, as the glucosides do not reduce Fehling’s solution and do not form osazones. They probably contain some such grouping as:

$CH_2OH.(CHOH)_3.CH \overset{\diagup O \diagdown}{\text{---}} CH.O.B$, in which B represents the benzenic component.

The glucosides are decomposed (hydrolyzed) by heating with dilute acids, or, at very slightly elevated temperatures, by certain enzymes, such as **emulsin**, which exists in almonds, **myrosin**, in mustard seeds, the **invertin** of malt, and salivary and intestinal enzymes. They are very slowly hydrolyzed by heating with water under pressure, if at all; and only a few of them are decomposed by alkalies.

The glucosides yielding pentoses on hydrolysis are more properly designated **pentosides**.

Phenyl Glucosides—Glucosyl phenate— $C_6H_{11}O_5.O.C_6H_5$ —is the simplest of the glucosides, and is an artificial product, formed by mixing alcoholic solutions of acetochlorhydrose and potassium phenate:

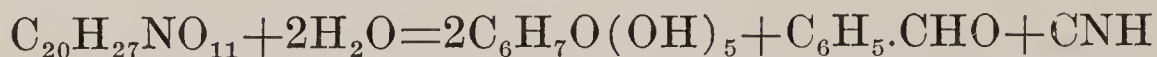


It forms soluble, crystalline needles, fusible at 172° , and is decomposed by emulsin into glucose and phenol.

Among the more important of the natural glucosides are the following:

Æsculin— $C_{15}H_{16}O_9$ —which exists in the rinds of horse-chestnuts. It forms colorless crystals, sparingly soluble in water, the solutions having a brilliant blue fluorescence, even when very dilute. It forms a yellow solution with HNO_3 , which becomes deep blood-red on supersaturation with ammonia. It is decomposed by dilute mineral acids, or by emulsin, into glucose and **æsculetin**, $C_9H_6O_4$, which is probably a dioxy-derivative of coumarin: $C_6H_2(OH)_2$ $\begin{array}{l} \nearrow CH:CH \\ \searrow O-CO \end{array}$

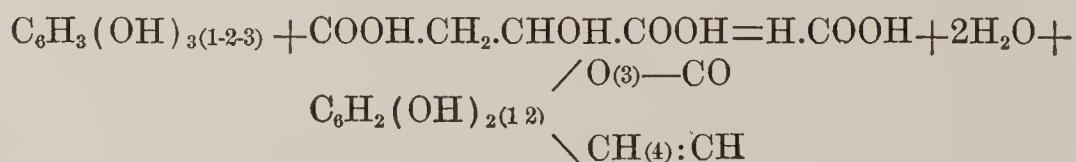
Amygdalin— $C_{20}H_{27}NO_{11}$ —exists in the bitter almond, in the kernels of peach- and plum-pits, apple- and pear-seeds, and a great variety of other plants. It crystallizes in colorless prisms with 3 Aq, easily soluble in water, insoluble in ether, odorless, and bitter. It is decomposed by dilute mineral acids, or by emulsin, into two molecules of glucose and one each of benzoic aldehyde and hydrocyanic acid:



By the action of alkalies, particularly by heating with $Ba(OH)_2$, amygdalin yields **amygdalic acid**, $C_{20}H_{28}O_{13}$, of which amygdalin appears to be the nitrile: $C_6H_7O(OH)_4 \cdot O \cdot C_6H_7O(OH)_3 \cdot O \cdot CH(C_6H_5)CN$ and this, on splitting off of the sugar, first forms the nitrile of mandelic acid: $C_6H_5 \cdot CHOH \cdot CN$, the subsequent decomposition of which into $C_6H_5 \cdot CHO$ and HCN is evident. Amygdalin itself is non-poisonous, but its ready decomposition, with formation of the extremely poisonous hydrocyanic acid, is a prolific source of cyanic poisoning.

Coniferin— $C_{16}H_{22}O_8$ —is a glucoside occurring in the inner bark (cambium) of coniferous plants, and in asparagus and the sugar-beet. It crystallizes in silky, white needles, sparingly soluble in water, faintly bitter. With phenol and concentrated hydrochloric acid it assumes an intense blue color (pine-shaving reaction). It is decomposed by emulsin into glucose and coniferyl alcohol, which is a hydroxyl-oxymethyl cinnamyl alcohol: $CH_3 \begin{array}{l} HO \\ \text{---} O \end{array} \nearrow C_6H_3 \cdot CH:CH \cdot CH_2OH$. By oxidation with chromic acid it forms **glucovanillin**, $C_6H_{11}O_5 \cdot O \cdot C_6H_3(OCH_3)CHO$, which is decomposed by emulsin into glucose and vanillin: methylprotocatechuic aldehyde. Glucovanillin, containing an aldehyde group, forms a crystalline compound with phenylhydrazine, and an oxime. By further oxidation it forms **glucovanillic acid**, and by reduction, the corresponding alcohol.

Daphnin, $C_{15}H_{16}O_9$, occurs in the bark of *Daphne mezereum*, and other species of *Daphne*. It crystallizes in colorless prisms, bitter and astringent, sparingly soluble in water and in ether, soluble in alcohol. It is colored bluish by ferric chloride. It is decomposed into glucose and **daphnetin**, $C_9H_6O_4$, isomeric with æsculetin (above). Daphnetin has been shown to be a dioxycoumarin, having the hydroxyls in the positions 1, 2, by its synthesis by condensation of pyrogallol and malic acid:



Digitalis Glucosides.—The active substance of digitalis consists, in part at least, of a glucoside, or glucosides, probably accompanied by products of decomposition, but the chemistry of these compounds requires further investigation. **Digitonin**, $C_{27}H_{44}O_{13}(?)$, is the most abundant constituent of the “amorphous digitalins,” and has little or no therapeutic value. It is an amorphous, white solid, very soluble in water, which crystallizes from its alcoholic solutions. It is decomposed by dilute hydrochloric acid into **digitonein**, or **digitogenin**, $C_{15}H_{24}O_4$, glucose and galactose. **Digitalin**, $(C_5H_8O_2)_n(?)$, separates in amorphous or nodular masses from its alcoholic solution. On decomposition it yields **digitaliresin**, $C_{16}H_{22}O_2$, glucose and **digitalose**, $C_7H_{14}O_5$. It has the physiological action of digitalis upon the heart, and is the principal constituent of “Homolle’s digitalin.” **Digitoxin**, $C_{21}H_{32}O_7(?)$, crystallizes in fine needles, insoluble in water, soluble in hot alcohol and in chloroform. It is the most actively poisonous of the digitalis glucosides, and is the chief constituent of “Nativelle’s digitalin.” Digitalin gives a color-reaction which is not given by digitoxin: it forms a golden-yellow or brownish solution with concentrated H_2SO_4 , which becomes violet-red by the action of bromine vapor.

Toxicology.—The prominent *symptoms* of poisoning by digitalis are: nausea, and occasionally vomiting; sometimes colic and diarrhea; after two or three hours, marked diminution in the frequency of the pulse, which may fall to 40 or even 25; dyspnea, attended by a sense of oppression in the chest and coldness of the extremities; headache, vertigo, and tendency to sleep; usually attacks of syncope occur, provoked sometimes by the slightest movement of the patient; death is generally by syncope, sometimes after several hours of coma succeeded by convulsions.

The *treatment*: The patient must be kept strictly in the recumbent position. The stomach should be washed out with infusion of tea by the stomach tube. Stimulants should be given.

Indican— $C_{26}H_{31}NO_{17}$ —is a glucoside occurring in the indigo plant. It is a yellow or light brown syrup, which cannot be dried without decomposition, bitter and disagreeable in taste, acid in reaction, and soluble in water, alcohol and ether. It is very prone to decomposition. Even slight heating decomposes it into leucine, **indicanin**, $C_{20}H_{23}NO_{12}$, and **indiglucin**, $C_6H_{10}O_6$. A characteristic decomposition is that by which it yields indigo-blue and indiglucin, along with other products:



The substance found in the urine, and erroneously called “indican,” is not a glucoside, but is potassium indoxyl sulphate: $K.C_8H_6N.SO_4$ (see p. 417).

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, exists in the seeds of black mustard as its K salt, which is hydrolyzed by myrosin into glucose, allyl isothiocyanate and $KHSO_4$.

Phloridzin, $C_{21}H_{24}O_{10}$, occurs in the root-bark of apple and other fruit trees. When ingested it causes glycosuria. It is hydrolyzed by boiling with dilute acids, or even with water, into a crystalline, dextrogyrous hexose, **phlorose**, and **phloretin**, $C_{15}H_{14}O_5$, which is further decomposed by hot alkalies into phloroglucin and **phloretic**, or **p-oxyhydratropic acid**: $C_6H_4(OH).C_2H_4.COOH$.

Salicin— $C_{13}H_{18}O_7$ —occurs in willow bark. It is a white, crystalline substance, insoluble in ether, soluble in water and in alcohol, very bitter in taste. Concentrated H_2SO_4 colors it intensely red, the color being discharged by addition of water. It is decomposed by emulsin, by saliva, or by mineral acids into glucose and saligenin. When taken into the economy it is converted into salicylic aldehyde and acid, which are eliminated in the urine. **Populin**, a glucoside from poplar bark, is benzoyl-salicin.

Santonin— $C_{15}H_{18}O_3$ is the active glucoside of the *Artemisia pauciflora*. It is used as an anthelmintic.

Solanin— $C_{42}H_{87}NO_{15}(?)$ —is a glucoside having basic properties, an alkaloid-glucoside, occurring in a variety of plants of the genus *Solanum*. It crystallizes in white, silky needles, acrid and bitter in taste, insoluble in water, sparingly soluble in alcohol and in ether. By the action of hot dilute acids it is decomposed into glucose and a basic substance, **solanidin**.

ANHYDRIDES AND ACID HALIDES.

The aromatic acidyls form oxides, or anhydrides, and haloid compounds, corresponding to those of the aliphatic acidyls, and produced by similar methods.

Benzoic Anhydride— $(C_6H_5.CO)_2O$ —is formed from benzoyl chloride by several methods: as by a reaction between benzoyl chloride and silver benzoate:



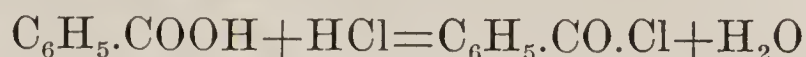
It is a crystalline solid, f. p. 42° , b. p. 360° .

Phthalic Anhydride— $C_6H_4(CO)_2O$ —being formed from a dicarboxylic acid, is produced from a single molecule of the acid, with elimination of H_2O . It is formed by fusing phthalic acid. It sublimes in needles; f. p. 128° ; sparingly soluble in cold water, soluble in hot water, with regeneration of the acid, very soluble in alcohol and in ether. It combines with phenols to form phthaleïns.

Salicylic Anhydride—Salicylide— $C_6H_4 \begin{smallmatrix} \diagup CO.O \\ \diagdown O.CO \end{smallmatrix} C_6H_4$ (probably)—is formed by the action of phosphorus oxychloride on salicylic acid. It forms a crystalline compound with chloroform in which the latter behaves as water of crystallization: $(C_7H_4O_2)_4.2CHCl_3$, which is utilized to purify that anesthetic.

Benzoyl Chloride— $C_6H_5.CO.Cl$ —was the first obtained of the

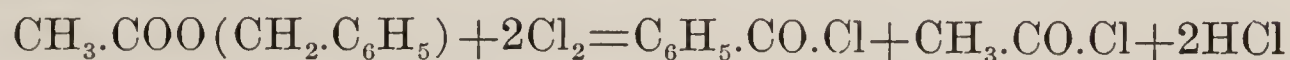
acidyl halides. It is formed by the action of hydrochloric acid upon benzoic acid, in presence of phosphorus pentoxide:



Or by the action of chlorine upon benzoic aldehyde:



Or, along with acetyl chloride, by the action of chlorine upon benzyl acetate:

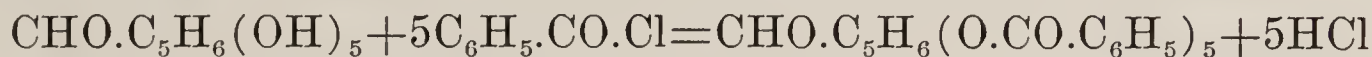


The two chlorides are separated by fractional distillation.

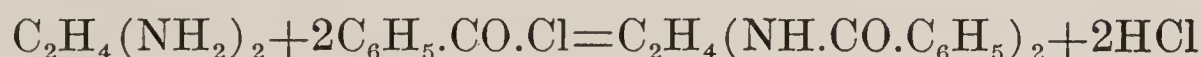
Benzoyl chloride is a colorless liquid; b. p. 198° ; having a penetrating odor. With silver (or mercuric) cyanide it forms benzoyl cyanide:



It acts readily upon the polyatomic alcohols and upon the hexoses, when shaken with their solutions in presence of caustic soda. With the hexoses pentabenzoyl compounds are formed, and crystallize out:



This is a reaction utilized for the isolation of hexoses and polyatomic alcohols. A similar reaction, similarly utilized, occurs with the diamines, in which insoluble, crystalline, dibenzoyl compounds are formed:



AROMATIC SULPHUR-DERIVATIVES—SULPHONIC ACIDS.

Many thio-aromatic compounds are known, as thiophenol, $\text{C}_6\text{H}_5\text{-SH}$, phenyl sulphide, $(\text{C}_6\text{H}_5)_2\text{S}$, and thio-benzoic acid, $\text{C}_6\text{H}_5.\text{COSH}$. But the most important of the aromatic compounds containing sulphur are the

Sulphonic Acids (p. 286), monobasic acids containing the group SO_3H , formed by the union of the aromatic hydrocarbon, or derivative, with H_2SO_4 with elimination of OH from the acid and H from the aromatic compound, a process called "sulphonation": $\text{C}_6\text{H}_6 + \text{H}_2\text{SO}_4 = \text{C}_6\text{H}_5.\text{SO}_3\text{H} + \text{H}_2\text{O}$. The aromatic and polybenzenic sulphonic acids are formed much more readily than the corresponding aliphatic acids, and, being acid and soluble, are largely used as dyes. They are usually produced by the action of fuming H_2SO_4 upon the aromatic compound, with or without the aid of heat.

The sulphonic acids are not decomposed by boiling with alkaline solutions, but their salts, when fused with caustic alkalies, yield phenols:



Distilled with potassium cyanide they yield nitriles:



By the action of PCl_5 they are converted into their chlorides, *e.g.*, $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{Cl}$, which may be, in turn, converted into **sulphinic acids, sulphones**, etc. They are easily soluble in water, and may be separated from their solutions, as sodium salts, by the addition of NaCl .

Benzene-monosulphonic Acid— $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$ —is formed by dissolving benzene in weak fuming sulphuric acid at a slightly elevated temperature, and diluting with H_2O . It crystallizes in extremely soluble, deliquescent plates with $1\frac{1}{2}$ Aq. By the action of PCl_5 upon benzene monosulphonates, **benzene sulphochloride** is produced:



This is an oily liquid, b. p. 246° , which is a valuable reagent for amines and amido compounds.

Three **benzene-disulphonic acids**— $\text{C}_6\text{H}_4(\text{SO}_3\text{H})_2$ —ortho-, meta- and para-, are known, also one **benzene-trisulphonic acid**— $\text{C}_6\text{H}_3(\text{SO}_3\text{H})_3$.

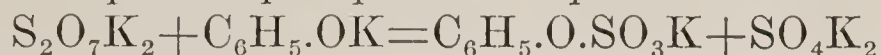
Three **toluene-sulphonic acids**— $\text{C}_6\text{H}_4(\text{CH}_3)\cdot\text{SO}_3\text{H}$ —ortho-, meta- and para-, have been obtained. By the action of a mixture of ordinary and fuming sulphuric acids upon toluene at a temperature not exceeding 100° , a mixture of the ortho- and para- acids is produced. When this is treated with PCl_5 , it is converted into a mixture of **para- and ortho-toluene sulphonic chlorides**— $\text{C}_6\text{H}_4\cdot\text{CH}_3\cdot\text{SO}_2\text{Cl}$. The ortho-chloride, when acted on by dry ammonia and ammonium carbonate, is converted into **ortho-toluene sulphamide**— $\text{C}_6\text{H}_4\cdot\text{CH}_3\cdot\text{SO}_2\text{NH}_2$. This product, when oxidized by potassium permanganate, is converted into **benzoyl-sulphonic imide**— $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{SO}_2\text{NH}$ —**benzosulphinidium**, or **benzosulphinide** or **saccharin** of the U. S. P.—an odorless, crystalline powder, having great sweetening power, its sweet taste being still detectable in a dilution of 1–50,000. Sparingly soluble in water and in ether, readily in alcohol. Its solutions are acid in reaction. When heated with Na_2CO_3 it is carbonized and gives off the odor of benzene. It is not attacked by H_2SO_4 .

Another series of sulphonic derivatives is obtained from the phenols. Among them is:

Ortho-phenol sulphonic Acid—**Sozolic acid**—**Aseptol**— $\text{C}_6\text{H}_4(\text{OH})_{(1)}(\text{SO}_3\text{H})_{(2)}$ which is prepared by the action of cold concentrated H_2SO_4 upon phenol. It is a reddish, syrupy liquid, soluble in H_2O in all proportions, has a faint and not disagreeable odor. It prevents fermentation and putrefaction, and is a non-poisonous, non-irritant antiseptic. The salts of this and the corresponding para- and meta-acids have been used as antiseptics and insecticides, under the name of **sulphocarbolates** or **phenol-sulphonates**, *e.g.* **Sodii phenolsulphonas** (U. S. P.).

Phenylsulphuric Acid—**Monophenyl Sulphate**— $\text{C}_6\text{H}_5\text{O} \diagup \text{SO}_2$ —isomeric with the phenol monosulphonic acids, and corresponding to

the acid ethyl sulphuric ester, ethylsulphuric acid, is the acid phenyl sulphuric ester which exists in its salts in the urine, and is the type of numerous similar compounds, the "ester sulphates," which are formed in the economy from substances containing a phenolic hydroxyl. The potassium salt of the acid is obtained by the action of potassium pyrosulphate upon potassium phenate:



The free acid decomposes rapidly.

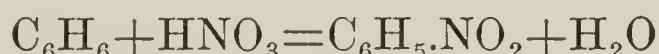
NITROGEN-CONTAINING DERIVATIVES OF BENZENE.

The nitrogen derivatives of benzene are very numerous, of great variety of structure, and include among their number several substances of great industrial value.

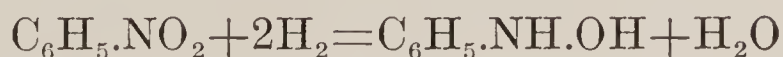
They may be classified into five principal groups: (1) The **nitro-compounds**, derived from other benzenic compounds by substitution of NO_2 for H, and the **nitroso-compounds**, containing the nitroso group, NO; (2) the **hydroxylamine compounds**, containing the group $\text{—N} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{H} \end{smallmatrix}$, and their nitroso derivatives; (3) the **amido-** and **imido-compounds**, containing NH_2 and NH , the **aromatic amines**, **amides**, and **amido-acids**, and their derivatives; (4) the **azo-** and **diazo-compounds** and their numerous derivatives, containing the grouping —N=N— ; (5) the **hydrazines**, containing the grouping =N—N= , and their nitroso derivatives.

NITRO- AND NITROSO-COMPOUNDS

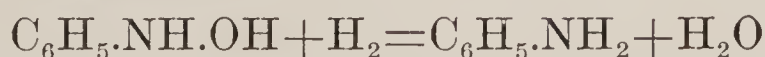
Nitro-benzenes.—These contain the nitro group directly attached to the carbon of the benzene ring. They are produced by the action of fuming HNO_3 , or a mixture of HNO_3 and H_2SO_4 , upon the hydrocarbons:



They are yellow liquids, sparingly soluble in water. Their most important property is their ready reduction, first to hydroxylamine compounds:



and then to amido-compounds:



Mono-nitro-benzene—Nitro-benzol—Nitro-benzene—Essence of Mirbane— $\text{C}_6\text{H}_5.\text{NO}_2$ —is obtained by the moderated action of fuming HNO_3 , or of a mixture of HNO_3 and H_2SO_4 on benzene.

It is a yellow, sweet liquid, with an odor of bitter almonds; sp. gr. 1.209 at 15° ; boils at 213° ; almost insoluble in water; very soluble in alcohol and in ether. Concentrated H_2SO_4 dissolves, and, when boiling, decomposes it. Boiled with fuming HNO_3 it is con-

verted into **dinitro-benzenes**. It is converted into aniline by reducing agents.

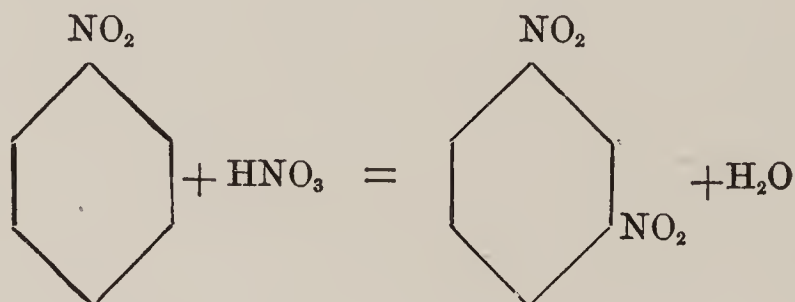
It has been used in perfumery as *artificial essence of bitter almonds*; but as inhalation of its vapor, even largely diluted with air, causes headache, drowsiness, difficulty of respiration, cardiac irregularity, loss of muscular power, convulsions, and coma, its use for that purpose is to be condemned. Taken internally, it is an active poison.

Nitro-benzene may be distinguished from oil of bitter almonds (benzoic aldehyde) by H_2SO_4 , which does not color the former; and by the action of acetic acid and iron filings, which convert nitro-benzene into aniline, whose presence is detected by the reactions for that substance (p. 371).

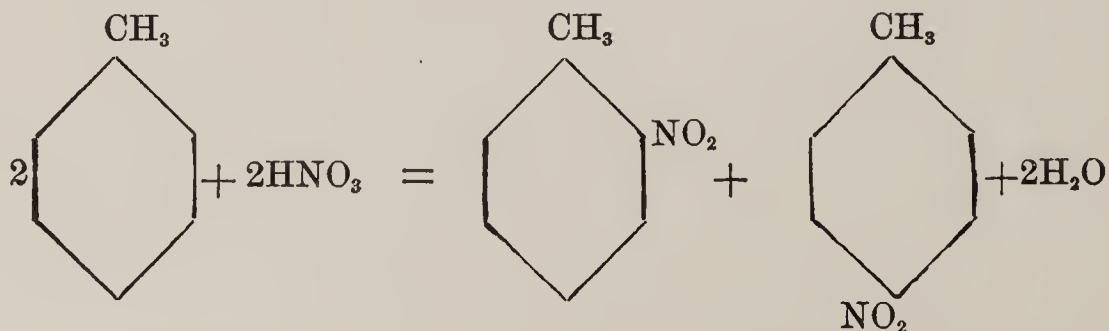
Dinitrobenzenes.—The three dinitrobenzenes are produced by boiling the mono-nitro compound with fuming HNO_3 . The meta-compound predominates, and may be separated by fractional crystallization from alcohol. It crystallizes in plates, fusible at 90° , and is used in the preparation of certain dyes, and of explosives, such as **roburite**, **sicherheit**, etc. The gases resulting from such explosives are poisonous.

Nitrotoluenes.— $\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$ —The o- and p-compounds are produced together by nitration of toluene, and exist in the commercial nitro-benzene. They may be separated by fractional distillation, the o-compound boiling at 218° , and the p- at 230° . By reduction they yield the corresponding toluidines, largely used in the color industry.

By the action of HNO_3 on nitrobenzene, meta-compounds are obtained principally:



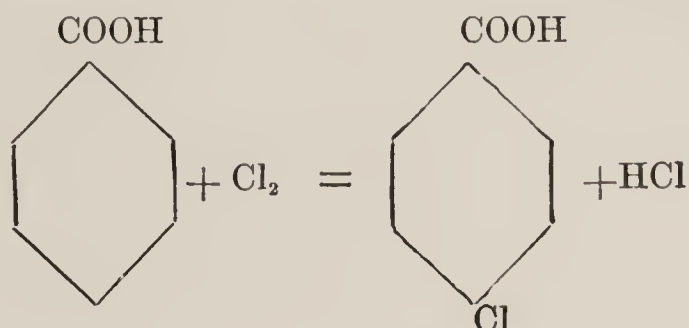
And by action of HNO_3 on toluene, we obtain a mixture of ortho- and para-nitrotoluene:



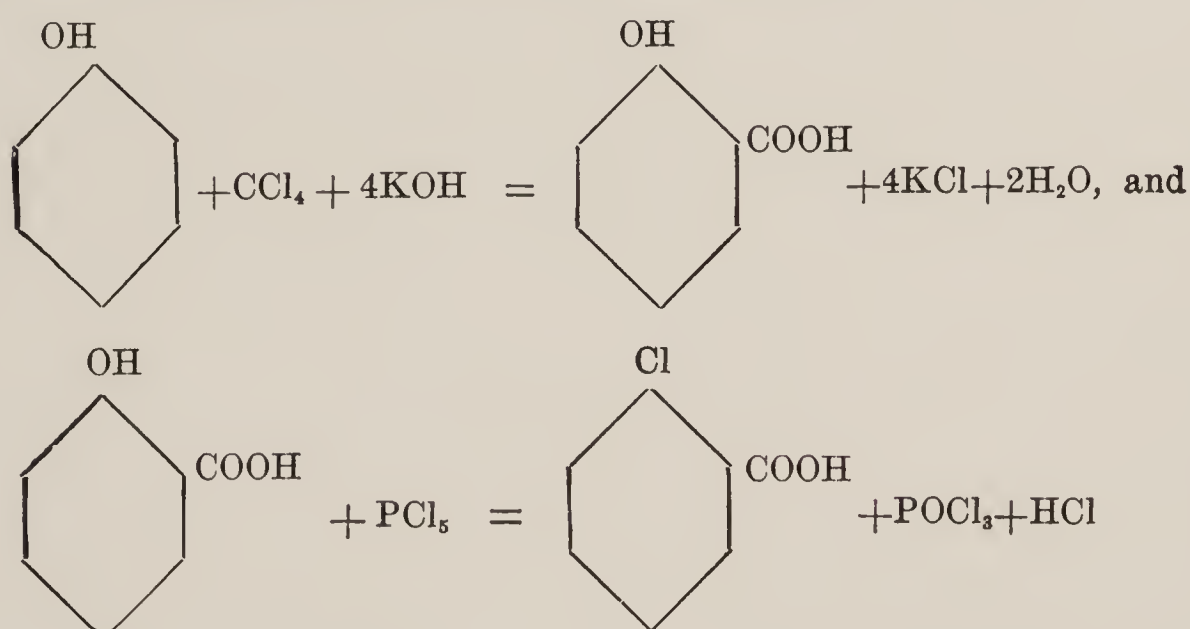
When the first substituted group contains a double or triple linkage as in NO_2 , COOH , CHO , COCH_3 , CN , a second introduced group

occupies the meta-position preferably. But when the first substituted group contains only single linkages as in Cl, Br, I, CH₃, NH₂, OH, mixtures of ortho- and para- groups are formed.

Thus by the action of Cl on benzoic acid the meta-compound alone is formed:



If ortho- or para-compound is desired, circuitous methods must be followed. Thus, for ortho acid, starting from phenol:



Nitro-phenols — Mononitro-phenols — C₆H₄(NO₂)OH — (1—2), (1—3) and (1—4) are formed by the action of HNO₃ on C₆H₅.OH. The **ortho** compound (1—2) crystallizes in large yellow needles, sparingly soluble, and capable of distillation with steam. The **meta** and **para** compounds are both colorless, non-volatile, crystalline bodies. Methyl chloride converts nitrophenols into the corresponding **nitro-anisols**, C₆H₄.OCH₃.NO₂, and ethyl iodide into **nitrophenetols**, C₆H₄.OC₂H₅.NO₂, which by reduction yield **anisidines** and **phenetidines** (p. 373). Two **dinitro-phenols**, (C₆H₃.OH(NO₂)₂)₍₂₋₄₎, and C₆H₃.OH(NO₂)₂ (2-6) are obtained by the action of strong nitric acid on phenol or on ortho- or para-mononitro phenol. They are both solid, crystalline substances, converted by further nitration into picric acid.

Trinitro-phenols—C₆H₂(NO₂)₃OH.—Two are known; (1) **Picric acid**—**Carbazotic acid**—**Trinitro-phenic acid**—(NO₂) in 2—4—6. It is formed by nitration of phenol, or of 1—2—4 or 1—2—6 dinitro-phenols, and also by the action of HNO₃ on indigo, silk, wool, resins, etc. It crystallizes in yellow plates or prisms, odorless, intensely bitter; acid in reaction; sparingly soluble in water, very soluble in

alcohol, ether, and benzene; it fuses at 122.5° , and may, if heated with caution, be sublimed unchanged; but, if heated suddenly or in quantity, it explodes with violence. It behaves as a monobasic acid, forming salts, which are for the most part soluble, yellow, crystalline, and decomposed with explosion when heated.

Picric acid colors silk and wool yellow. It is used as a reagent for the alkaloids, with many of which it forms crystalline precipitates, as it also does with many other substances. It is sometimes added to beer and to other food articles, to communicate to them either a bitter taste or a yellow color. Its solutions give yellow, crystalline precipitates with K salts; green precipitates with ammoniacal CuSO_4 ; and an intense red color when warmed with alkaline KCN solution. It is poisonous,

Nitro-cresols— $\text{C}_6\text{H}_3.\text{CH}_3.\text{OH}.\text{NO}_2$ —The o- and p- compounds are known. They are readily converted into the corresponding dinitro compounds, $\text{C}_6\text{H}_2.\text{CH}_3.\text{OH}.\text{(NO}_2)_2$. The 2-6 dinitro compound is used as a dye in the form of its sodium salt, under the name *Victoria orange*, or *saffron surrogate*. It is poisonous.

The **nitroso-phenols** are obtained by the action of nitrous acid upon the phenols; or by the action of hydroxylammonium chloride upon the quinones.

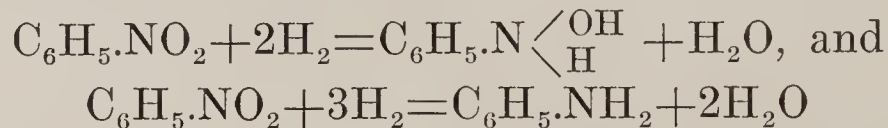
p-Nitroso-phenol — Quinoxime — $\text{C}_6\text{H}_4.\text{(OH)}_{(1)}\text{(NO)}_{(4)}$, or C_6H_4 $\begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{N.OH} \end{array}$ crystallizes in needles, and explodes when heated. **Dinitroso-resorcinol**— $\text{C}_6\text{H}_2(\text{OH})_{2(1,3)}(\text{NO})_{2(4,6)}$ is a brown, explosive substance, used as a green dye, *solid green*.

Nitro-acids, such as o-, m-, and p-nitro-benzoic acids, $\text{C}_6\text{H}_4\text{COOH}.\text{NO}_2$, etc., are known. They yield amido-acids by reduction.

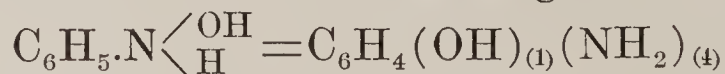
HYDROXYLAMINE COMPOUNDS.

Compounds derived from hydroxylamine by substitution of phenyl or alkyl-phenyls for extra-hydroxyl hydrogen are formed as intermediate products of reduction of the nitro-benzenes (p. 367).

Phenylhydroxylamine— $\text{C}_6\text{H}_5.\text{N} \begin{array}{c} \diagup \text{OH} \\ | \\ \diagdown \text{H} \end{array}$ —is an intermediate product of reduction between nitro-benzene and amido-benzene:



It is readily oxidized to nitroso-benzene and other products, and it reduces Fehling's solution and ammoniacal AgNO_3 solution. Mineral acids cause its intramolecular rearrangement to p-amido-phenol:



With nitrous acid it forms a nitroso derivative: $\text{C}_6\text{H}_5.\text{N} \begin{array}{c} \diagup \text{OH} \\ | \\ \diagdown \text{NO} \end{array}$. It is a crystalline solid; f. p. 81° ; and forms a crystalline, colorless hydrochloride.

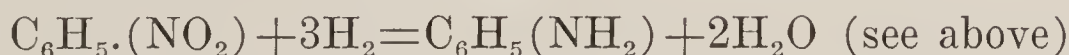
AMIDO-COMPOUNDS.

The **amido-benzenes** are the counterparts of the aliphatic primary monamines. They are obtained by reduction of the corresponding nitro-compounds. The reaction is, with moderate reduction, not so simple as is expressed by the equation:



but several important intermediate products are formed (p. 367, and above).

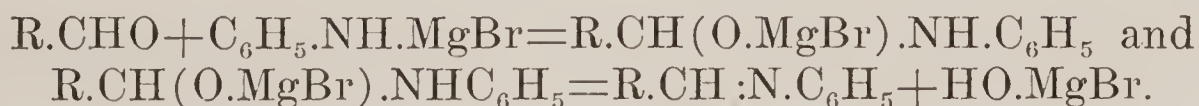
Aniline—Amido-benzene—Amido-benzol—Phenylamine — $\text{C}_6\text{H}_5.\text{NH}_2$ —exists in small quantity in coal-tar, and is one of the products of the destructive distillation of indigo. It is prepared by the reduction of nitro-benzene by hydrogen:



the hydrogen being liberated in the nascent state in contact with nitro-benzene by the action of iron filings on acetic acid.

Pure aniline is a colorless liquid; has a peculiar, aromatic odor, and an acrid, burning taste; sp. gr. 1.02 at 16° ; boils at 184.8° ; crystallizes at -8° ; soluble in 31 parts of cold water, soluble in all proportions in alcohol, ether, carbon bisulphide, etc. When exposed to air it turns brown, the color of the commercial “aniline oil,” and, finally, resinifies. It is neutral in reaction. Oxidizing agents convert it into rosaniline, $\text{C}_{20}\text{H}_{19}\text{N}_3$, from which blue, violet, red, green, or black derivatives are obtained. Cl, Br, and I act upon it violently to produce products of substitution. Concentrated H_2SO_4 converts it, according to the conditions, into **sulphanilic**, or **p-amido-benzene sulphonic acid**, $\text{C}_6\text{H}_4(\text{NH}_2)_{(1)}(\text{SO}_3\text{H})_{(4)}$, or **disulphanilic acid**, or **aniline 2-4 disulphonic acid**, $\text{C}_6\text{H}_3(\text{NH}_2)_{(1)}(\text{SO}_3\text{H})_{2(2,4)}$. With acids it unites, after the manner of ammonia, to form salts, most of which are crystallizable, soluble in water, and colorless, although by exposure to air, especially if moist, they turn red. The sulphate has been used medicinally. Potassium permanganate oxidizes it to nitro-benzene. Heated with H_2SO_4 and glycerol it produces quinoline, and substituted quinoline may be obtained by a similar reaction from substituted anilines.

With alkyl magnesium iodides and bromides, aniline and methyl aniline produce the Meunier compounds: $\text{C}_6\text{H}_5.\text{NH}.\text{MgBr}$. and $\text{C}_6\text{H}_5.\text{N}(\text{CH}_3).\text{MgBr}$. The former reacts with aldehydes to produce imines:



Aniline itself, when taken in the liquid form or by inhalation, is an active poison, producing symptoms similar to those caused by

nitro-benzene (p. 368). Its salts, if pure, seem to have but slight deleterious action.

Aniline may be recognized by the following reactions: (1) With a nitrate and H_2SO_4 : a red color; (2) cold H_2SO_4 does not color it alone; on addition of potassium dichromate, a fine blue color is produced, which, on dilution with water, passes to violet, and, if not diluted, to black. (3) With calcium hypochlorite: a violet color; (4) heated with cupric chlorate: a black color; (5) heated with mercuric chloride: a deep crimson color; (6) in very dilute solution (1:250,000), aniline gives a rose color with chloride of lime, followed by ammonium sulphhydrate.

Toluidines— $\text{C}_6\text{H}_4(\text{CH}_3)(\text{NH}_2)$ —Three toluidines, o-, m-, and p-, are known as the superior homologues of aniline. They occur in commercial aniline and play an important part in the production of aniline colors.

Xylidines—Amido-xylenes— $\text{C}_6\text{H}_3(\text{CH}_3)_2(\text{NH}_2)$.—Six compounds of this composition are known: two derived from ortho-xylene, three from meta-xylene, and one from para-xylene. Five of them exist in commercial xylidine.

The toluidines and xylidines yield products of substitution and addition similar to those of aniline.

Carbodiimides are substances having the general formula $\text{C} \begin{smallmatrix} // & \text{NR} \\ \backslash & \text{NR} \end{smallmatrix}$, in which RR are two univalent radicals, usually belonging to the aromatic series. They are prepared from the sulphureïdes, by loss of the elements of carbon oxysulphide, COS, by the action of heat or of oxidants.

Anilides.—These are compounds in which one of the H atoms of the amido group has been replaced by an acid radical. Or they may also be considered as amides, whose remaining hydrogen has been more or less replaced by phenyl, C_6H_5 .

Acetanilide — Antifebrine — Phenyl-acetamide — $\text{C}_6\text{H}_5(\text{NH}.\text{CO}.\text{CH}_3)$ —is obtained either by heating together aniline and glacial acetic acid for several hours, or, better, by the action of acetyl chloride on aniline. It forms colorless, shining, crystalline scales; fuses at 112.5° , and volatilizes unchanged at 295° . It is sparingly soluble in cold water, soluble in hot water and in alcohol.

When acetanilide is heated with an equal weight of ZnCl_2 , **flavaniline**, a colored substance having a fine green fluorescence, and soluble in warm dilute HCl, is produced.

Acetanilide and its derivatives in the urine respond to the **indophenol reaction**: Boiled a few minutes with HCl, a colorless solution is formed, which, on addition of H_2O and solution of phenol in chlorinated lime solution, assumes a turbid, dirty red color, and on addition of ammonia an indigo-blue color.

By the further substitution of a group (CH_3) in acetanilide, **methyl-acetanilide**, or **exalgine**, $\text{C}_6\text{H}_5.\text{N}(\text{CH}_3).\text{C}_2\text{H}_5\text{O}$, is produced. It is formed by the action of methyl-iodide upon sodium acetanilide, $\text{C}_6\text{H}_5.\text{NNa}.\text{C}_2\text{H}_5\text{O}$. It is a crystalline solid, sparingly soluble in H_2O , readily in dilute alcohol. Its odor is faintly aromatic.

The "aniline dyes" now so extensively used, even those made from aniline, are not compounds of aniline, but are salts of bases formed from it, themselves colorless, called rosaniline.

Phenylamines—Phenylenediamines, etc.—Aniline is the simplest representative of a large class of substances. It may be considered as benzene in which H has been replaced by NH_2 , thus: $\text{C}_6\text{H}_5.\text{NH}_2$. Its superior homologues, derivable from the superior homologues of benzene, each have at least three isomeres, ortho-, meta-, and para-, according to the orientation of the groups NH_2 and $\text{C}_n\text{H}_{2n+1}$. Aniline may also be considered as ammonia in which H has been replaced by phenyl, C_6H_5 , thus being a primary monamine $\text{C}_6\text{H}_5 \begin{smallmatrix} \text{H} \\ \text{H}_2 \end{smallmatrix} \text{N}$. The remaining two H atoms may be replaced by other radicals to form an almost infinite variety of **secondary** and **tertiary phenylamines**, precisely as in the case of the aliphatic monamines.

Phenylcarbylamine—Phenyl Isocyanide—Isobenzonitrile— $\text{C}_6\text{H}_5.\text{N}:\text{C}$ —is formed when chloroform is heated with aniline and caustic potash in alcoholic solution (p. 206). It is a liquid, having a most persistent, disagreeable odor. Nascent hydrogen converts it into methyl aniline. Heated to 220° , it is converted into its isomere, **benzonitrile**, or **cyanobenzene**, $\text{C}_6\text{H}_5.\text{CN}$, which is a liquid having an odor of bitter almonds; also formed by distilling potassium benzene sulphonate with potassium cyanide.

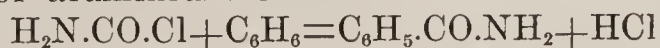
Amido-phenols— $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$ —Three are known, ortho-, meta-, and para-, obtained by the action of reducing agents upon the corresponding nitro-compounds. Their methylic ethers, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}(\text{CH}_3) \\ \text{NH}_2 \end{smallmatrix}$ are known as **anisidines**; and their ethylic ethers, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O}(\text{C}_2\text{H}_5) \\ \text{NH}_2 \end{smallmatrix}$ as **phenetidines**.

By the action of glacial acetic acid upon paraphenetidine, an aceto-derivative, **para-acetophenetidine**, $\text{C}_6\text{H}_4(\text{OC}_2\text{H}_5)_{(1)}.(\text{NH}.\text{C}_2\text{H}_3\text{O})_{(4)}$, is formed. It is used as an antipyretic, under the name **phenacetine**, and is a colorless, odorless, tasteless powder, sparingly soluble in H_2O , readily soluble in alcohol, fuses at 135° . Its hot aqueous solution is colored violet, changing to ruby-red, by chlorine water.

Aromatic acid amides are formed by methods similar to those by which the aliphatic amides are produced, and resemble them in their reactions (p. 312). Thus **benzamide**, or **benzoyl amide**, $\text{C}_6\text{H}_5.\text{CO}.\text{NH}_2$, is formed by the action of benzoyl chloride upon ammonia:



as a crystalline solid, fusible at 130° , or by the action of urea chloride upon benzene in presence of aluminium chloride:

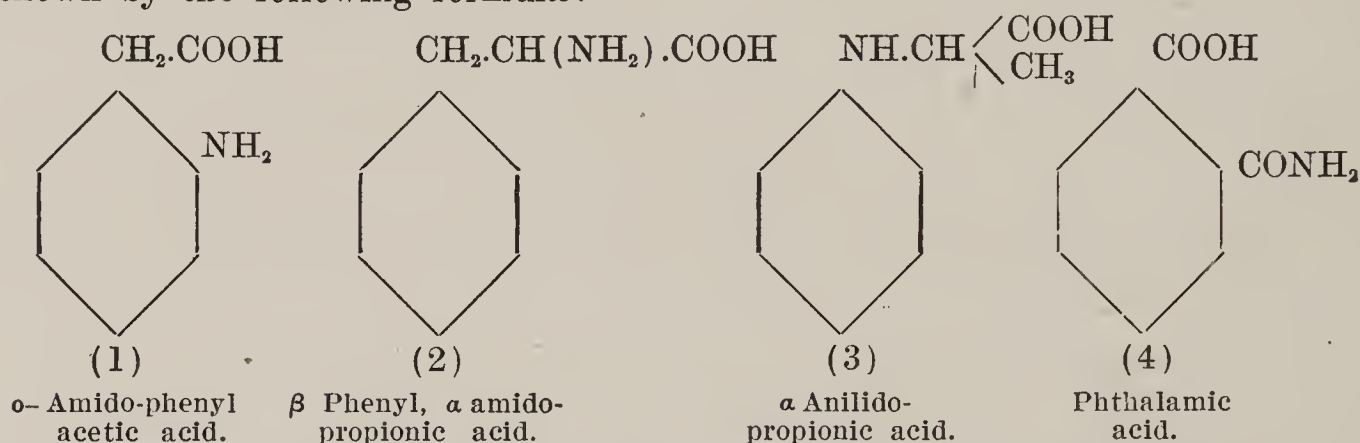


Two formulæ of benzamide are possible: the amide formula, $\text{C}_6\text{H}_5.\text{CO}.\text{NH}_2$, and the imide formula, $\text{C}_6\text{H}_5.\text{COH}:\text{NH}$. Derivatives corresponding to each are known.

Phthalamide— $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CONH}_2 \\ \text{CONH}_2 \end{smallmatrix}$, **phthalamic acid**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH} \\ \text{CONH}_2 \end{smallmatrix}$, and **phthalamide**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{NH}$ are obtained from phthalic anhydride. The last named may be indirectly condensed, through its imide H, with the fatty acids to produce compounds which serve as starting points in syntheses of diamido fatty acids.

The **aromatic amido-acids** greatly exceed the aliphatic (p. 321) in number and variety. They are : (1) **Amido-phenyl acids**, which may be considered

either as aromatic acids, in which a ring hydrogen atom (or atoms) has been replaced by NH_2 ; or as aliphatic acids, in which amido-phenyl ($\text{C}_6\text{H}_4.\text{NH}_2$)' has replaced H in a hydrocarbon group; (2) **phenyl-amido acids**, considered either as aromatic acids, in which NH_2 replaces H in a hydrocarbon group of a lateral chain, or as amido-aliphatic acids, in which phenyl (C_6H_5)' has been substituted for H in a hydrocarbon group; (3) **anilido-acids**—aliphatic amido-acids in which phenyl has been substituted for H in NH_2 . In this class are included the anilides of the dicarboxylic acids (p. 371), *e.g.*, **oxanilic acid**, $\text{OC} \begin{smallmatrix} \diagup \text{NH}(\text{C}_6\text{H}_5) \\ \diagdown \text{COOH} \end{smallmatrix}$; (4) **amic acids** (p. 310), derived from the dicarboxylic aromatic acids by substitution of NH_2 for OH in one carboxyl group. Besides these there are amido-acids referable to 1 and 3, in which the radical benzoyl, $\text{C}_6\text{H}_5.\text{CO}$, takes the place of phenyl, C_6H_5 . The structure of these several acids is shown by the following formulæ:



Those aromatic amido-acids in which the amido group is attached to the ring do not yield monochlor-acids by treatment with NOCl , but those in which the NH_2 is in a lateral chain do, as do also the amido-acids of the acetic and oxalic series (p. 323).

Amido-phenyl Acids, of which **anthranilic**, or ***o*-amido-benzoic acid**, $\text{C}_6\text{H}_4(\text{COOH})_{(1)}(\text{NH}_2)_{(2)}$, is the type, are formed by reduction of the corresponding nitro-benzoic acids. Nitrous acid converts them into the corresponding oxyacids. Thus anthranilic acid yields salicylic acid. The *o*-acids exhibit a great tendency to the formation of lactams, some of which are indigo deriva-

tives, as **oxindole**, the lactam of *o*-amido-phenyl acetic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}_2.\text{CO}_{(1)} \\ \diagdown \text{NH}_2 \end{smallmatrix}$

and **dioxindole**, the lactam of *o*-amido-mandelic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}(\text{OH})\text{CO}_{(1)} \\ \diagdown \text{NH}_{(2)} \end{smallmatrix}$

Isatin, a product of oxidation of indigo, is the lactam of *o*-amido-benzoyl-formic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO}.\text{CO}_{(1)} \\ \diagdown \text{NH}_{(2)} \end{smallmatrix}$ The **amido-cinnamic acids** are closely related to quino-

line.

Phenyl-alanine, is a **phenyl-amido acid**: β phenyl- α -amido-propionic acid (formula above), which exists in certain lupines, and is a product of decomposition of the proteins. Its corresponding *p*-oxyphenyl derivative is:

Tyrosine—*p*-Oxyphenyl alanine— $(\text{HO})_{(4)}\text{C}_6\text{H}_4.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}$ —one of the earliest known products of protein decomposition. Tyrosine is formed from proteins, particularly from casein, by the action of proteolytic enzymes, and during putrefaction, and is also formed from them by boiling with HCl or H_2SO_4 , or by fusion with KOH , always accompanied by leucine. It exists normally in the intestine, and pathologically in the urine. It has been formed synthetically, from phenyl-acetaldehyde, $\text{C}_6\text{H}_5.\text{CH}_2.\text{CHO}$, by conversion into phenyl-alanine, $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}$ and *p*-amido-phenyl- α -alanine, $\text{C}_6\text{H}_4(\text{NH}_2)_{(4)}\text{CH}_2.\text{CHNH}_2.\text{COOH}$. It crystallizes in silky needles, arranged in stellate bundles, very sparingly soluble in cold water, soluble in 150 parts of

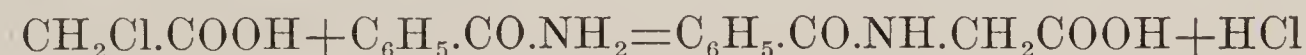
hot water, more soluble in the presence of acids or of alkalies, insoluble in alcohol and in ether. It unites with acids and bases to form salts. When heated it turns brown and gives off the odor of phenol; when heated to 270° , it is decomposed into CO_2 and **oxyphenylethyl-amine**, $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, which sublimes.

With H_2SO_4 , and slightly warmed, it dissolves with a transient red color; the solution, cooled, diluted, neutralized with BaCO_3 , and filtered, gives a violet color with FeCl_3 (Piria's reaction). When moistened with HNO_3 and slowly evaporated, it leaves a yellow residue, which forms a deep reddish-yellow color with NaOH (Scherer's reaction). Heated with water and a few drops of Millon's reagent it gives a red liquid, and forms a red precipitate (Hofmann's reaction). It gives the diazo reaction.

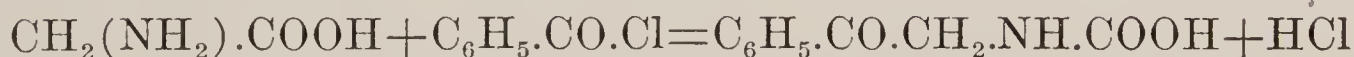
p-Amidophenyl- α -alanine— $\text{NH}_2(\text{p})\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH}$ —produced by reduction of p-nitrophenyl-alanine, is both a phenyl-amido and an amido-phenyl acid.

Anilido Acids derived from the monocarboxylic acids are produced by the action of the monochlor-acids upon aniline, as the aliphatic amido-acids are obtained from ammonia. Thus monochloroacetic acid and aniline yield **anilido-acetic acid**, or **phenyl glycocoll**, $\text{CH}_2\text{Cl}\cdot\text{COOH} + \text{C}_6\text{H}_5\cdot\text{NH}_2 = \text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH} + \text{HCl}$.

Hippuric Acid—**Benzoyl-amido-acetic acid**—**Benzoyl glycocoll**— $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$ —is similarly obtained from monochloroacetic acid and benzamide:



It is also formed by the action of benzoyl chloride upon glycocoll in the presence of sodium hydroxide:



Hippuric acid exists in the urine of the herbivora; and in human urine in the daily quantity of 0.29–2.84 grams, and in larger amount when benzoic acid, cinnamic acid and other aromatic substances are taken. It crystallizes in prisms, colorless, odorless, bitter, sparingly soluble in water, readily soluble in alcohol, fuses at 187° . When heated with acids or alkalies it is decomposed into benzoic acid and glycocoll. Oxidizing agents convert it into benzoic acid, benzamide and carbon dioxide. When heated alone it gives off a sublimate of benzoic acid and the odor of hydrocyanic acid. Its ferric salt is insoluble, and is formed as a brown precipitate when FeCl_3 is added to its solution. Heated with lime it forms benzene and ammonia.

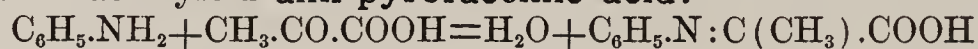
Anilic Acids are anilido acids corresponding to the dicarboxylic acids. They may be considered as being formed by substitution of the univalent remainder of the acid for H in aniline, and therefore as anilides (p. 372); or by substitution of phenyl for H in the NH_2 group of the amic acids. Thus **oxanilic acid**, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{COOH}$, corresponds to oxalic acid, $\text{COOH}\cdot\text{COOH}$, and to oxamic acid, $\text{CONH}_2\cdot\text{COOH}$.

Carbanilic Acid— $\text{O}:\text{C} \begin{smallmatrix} \text{OH} \\ \text{NH}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$ —the anilic acid corresponding to carbonic and carbamic acids, and isomeric with phenyl urethane (p. 314), is not known in the free state. Its esters, however, are known as **phenyl urethanes**. A great number of **phenyl-urea** and **phenyl-guanidine** derivatives are also known.

Related to the amido acids are the **hydroxamic acids** and the **anil acids**.

Hydroxamic Acids are derivable from the imide formula of benzamide (p. 373) by substitution of OH for H in the imide group. Thus **benzhydroxamic acid**, $\text{C}_6\text{H}_5.\text{C} \begin{smallmatrix} // \text{NOH} \\ \backslash \text{OH} \end{smallmatrix}$, corresponds to benzamide, $\text{C}_6\text{H}_5.\text{C} \begin{smallmatrix} // \text{NH} \\ \backslash \text{OH} \end{smallmatrix}$. Both H atoms in the OH groups are replaceable by alkyls to form esters. **Amidoximes** (p. 300) are derived from the hydroxamic acids by substitution of NH_2 for OH, *e.g.*, **benzenylamidoxime**, $\text{C}_6\text{H}_5.\text{C} \begin{smallmatrix} // \text{NOH} \\ \backslash \text{NH}_2 \end{smallmatrix}$.

Anil Acids are aniline derivatives of the ketone-carboxylic acids, formed by the union of aniline and the acid, with elimination of water. Thus aniline and pyroracemic acid yield **anil-pyroracemic acid**:



DIAZO, DIAZOAMIDO, AND AZO COMPOUNDS.

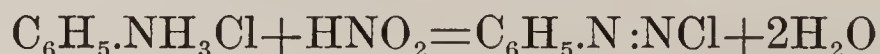
Diazo compounds contain the group —N:N— , united by one bond to an aromatic group, and by the other to an acid radical.

Diazoamido compounds contain the group —N:N.NH— , united to two aromatic groups.

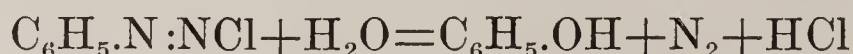
Azo compounds contain the group —N:N— , united to two aromatic hydrocarbon groups, or to one aromatic and one aliphatic hydrocarbon group.

Diazo Compounds—are derivatives of diazobenzene, $\text{C}_6\text{H}_5.\text{N}:\text{NH}$, which is, however, only known in compounds in which the imide H has been replaced by acidyls or halogens, or of other cyclic compounds having the structure R.N:N.X , in which R is a cyclic hydrocarbon radical and X an acidyl or a halogen. These diazo compounds are very unstable, decomposing explosively on slight elevation of temperature or by shock. They are therefore rarely isolated in their own form of crystalline solids, but, on the other hand, their instability, or reactivity, renders their formation as intermediate products very serviceable in the formation of synthetic products, and in the manufacture of the “azo dyes,” which include most of the so-called “aniline colors.” Their utility in this regard depends upon the facility with which the diazo group, .N:NX is displaced by other univalents, such as OH, H, CN, and halogens.

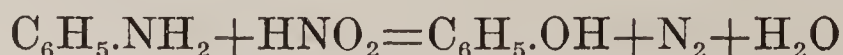
The diazo compounds are produced by the action at low temperature of HNO_2 upon the salts of the aromatic primary amines. Thus aniline chloride yields diazobenzene chloride:



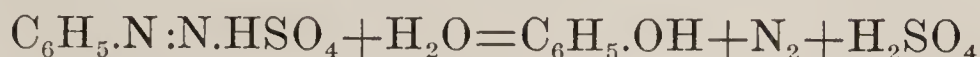
But if the temperature is allowed to rise the action proceeds further, with elimination of N and formation of a phenol:



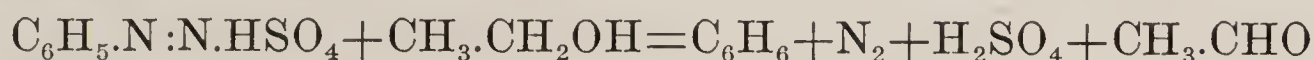
the sum of the reactions upon the amine being then the same as that of HNO_2 upon the aliphatic primary amines, *i.e.*, the substitution of OH for NH_2 , thus



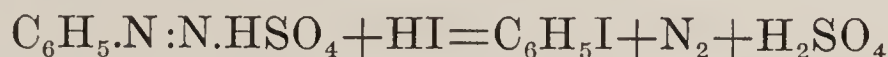
This method of formation and decomposition of the diazo compounds is frequently utilized for the introduction of hydroxyl into aromatic molecules, starting either from the hydrocarbon or intermediate forms of nitro or amido derivatives. The process is referred to as **diazotizing**. A similar decomposition is effected by simply boiling aqueous solutions of diazo compounds:



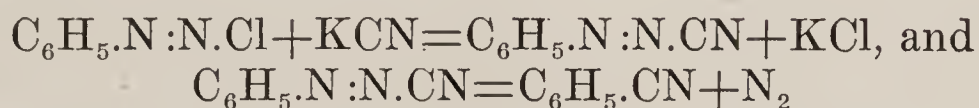
The replacement of the diazo group by H, with formation of the hydrocarbon, is effected by boiling with strong alcohol, which is oxidized to aldehyde:



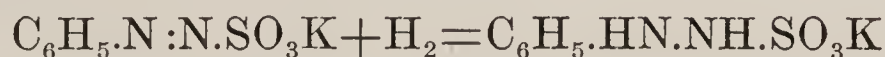
The hydracids bring about the substitution of halogen for the diazo group, with formation of a monohalide:



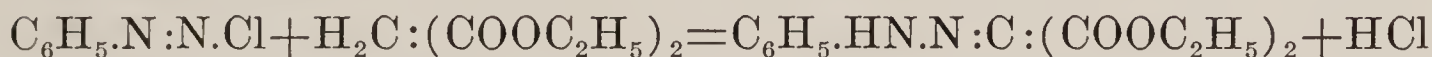
A similar decomposition is effected by CuCl , and by PtCl_4 or PtBr_4 . Diazobenzene chloride in presence of CuSO_4 is converted by KCN into diazobenzene cyanide, which then splits off N to form cyanobenzene:



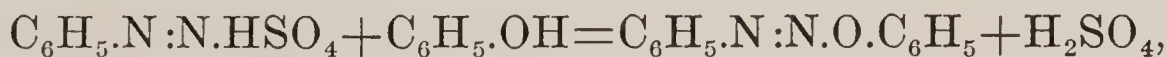
Notwithstanding the instability of the attachment of the diazo group, the diazo compounds also enter into reactions in which the N is not split off. Thus nascent hydrogen reduces the diazo salts to phenylhydrazine salts (p. 379):



With substances containing the grouping— $\text{CH}_2.\text{CO}$ —the diazo compounds react in alkaline solution to form hydrazones (p. 380), in which, however, the hydrazone group replaces H_2 , not O. Thus with the malonic ester:



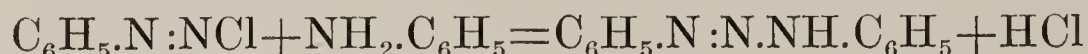
With the primary amines, whether aliphatic or aromatic, the diazo compounds form diazoamido- or disdiazamido compounds (below). With the phenols the diazo salts do not produce azoxy compounds (p. 378), but first diazo oxy compounds:



which suffer atomic transposition to form oxyazo compounds: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}_6\text{H}_4.\text{OH}$, as do the diazoamido compounds (below).

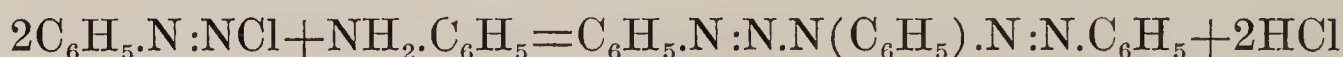
Diazoamido and Disdiazamido Compounds.—The diazoamido compounds, containing the group — $\text{N}:\text{N}.\text{NH}$ — united to two aromatic groups, are formed by the action upon each other of diazo salts and primary or secondary amines in equal molecular proportion.

Thus diazoamido benzene, $C_6H_5.N:N.NH.C_6H_5$, is formed, as a yellow, crystalline, explosive solid, insoluble in water, soluble in hot alcohol, by the action of diazobenzene nitrate, or chloride, upon aniline:



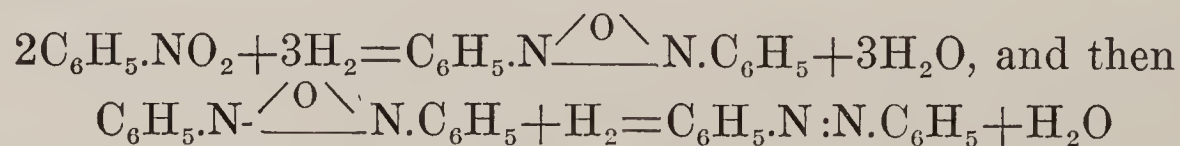
The most notable property of these substances is their transformation, by intramolecular rearrangement into the isomeric p-azo-amido compounds. Thus diazoamido benzene becomes p-azo-amido benzene, $C_6H_5N:NC_6H_4.(NH_2)_{(4)}$. This intramolecular transposition takes place slowly in the presence of traces of aniline salts, at the ordinary temperature.

The **disdiazamido** compounds, containing the group $-N:N.NH.N:N-$, are formed under the same conditions as the diazoamido compounds, except that two molecules of the diazo salts are taken for one of the amine:

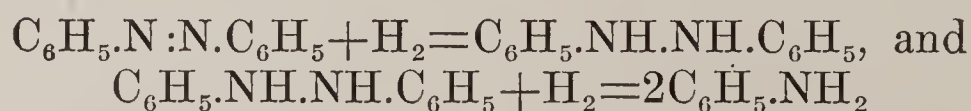


Azo Compounds.—The azo compounds contain the same group, $-N:N-$, as the diazo compounds, but they differ from the latter in that the two valences are both satisfied by hydrocarbon groups; either both aromatic, as in **azobenzene**, $C_6H_5.N:N.C_6H_5$, or one aromatic and one aliphatic, as in **benzene azo-methane**, $C_6H_5.N:N.CH_3$. They are “mixed,” “symmetric,” and “unsymmetric,” according as they contain an aromatic and an aliphatic group, or two like aromatic groups, or two unlike aromatic groups. In designating the orientation of substituted groups the $-N:N-$ attachments are considered as occupying the (1) position in both hydrocarbon groups, and the positions of substitution in one ring are indicated by 2, 3, etc., and those in the other by 2', 3', etc.

The azo compounds are formed: (1) By moderate reduction of nitro-aromatic compounds in alkaline solution. The reaction takes place in two stages, an **azoxy** compound being first formed and then further reduced. Thus nitro-benzene forms, first **azoxybenzene**, then azobenzene:



The reduction readily progresses further, and always does so in acid solutions, with formation, first of a **hydrazo** product (p. 379), and finally an amido derivative (pp. 371, 373). Thus azobenzene forms, first, **hydrazobenzene**, or symmetrical diphenyl hydrazine, and then aniline:



(2) By reduction of the azoxy compounds. (3) The amido derivatives of the azo hydrocarbons are technically manufactured by

molecular rearrangement of the diazoamido compounds (p. 378), or (4) by acting upon the tertiary anilines, or upon the m-diamines, with diazo salts.

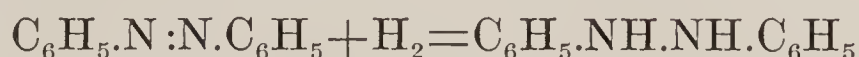
The azo compounds are much more stable than the diazo compounds. The hydrocarbons, such as **azobenzene**, $\text{C}_6\text{H}_5\text{.N:N.C}_6\text{H}_5$, are highly colored crystalline solids, which are not basic, and do not act as dyes. They are sparingly soluble in water, readily soluble in alcohol and in ether. Their most important derivatives are the amido-azo compounds, which are highly colored and strongly basic, crystalline solids, whose solutions have, however, no dyeing power. But they combine readily with salt-forming groups, notably to form sulphonic acids, which constitute many of the most extensively used "aniline dyes."

p-Amido-azobenzene — $\text{C}_6\text{H}_5\text{.N:N.(C}_6\text{H}_4\text{)(NH}_2\text{)}_{(4)}$ — prepared by the methods given above, is the starting point in the manufacture of several yellow, orange, and brown "diazo dyes," and of the "inuline dyes." It forms yellow needles, fusing at 123° .

HYDRAZINE COMPOUNDS.

The aromatic hydrazines are derived from diamide, $\text{H}_2\text{N.NH}_2$, by substitution of hydrocarbon or other aromatic radicals for one or more of the hydrogen atoms.

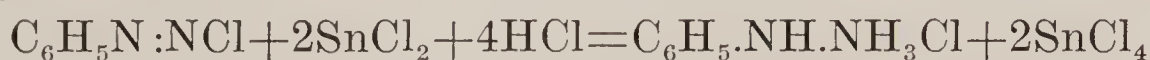
Hydrazo-benzene — sym. **Diphenyl-hydrazine** — $\text{C}_6\text{H}_5\text{.NH.NH.C}_6\text{H}_5$ — is obtained by moderate reduction, as with zinc dust or sodium amalgam, of azobenzene:



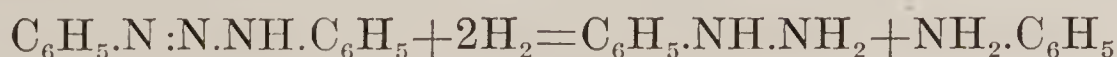
It forms colorless crystals, having the odor of camphor, fusible at 132° , insoluble in water, soluble in alcohol and in ether. It readily oxidizes to azobenzene. Strong reducing agents break it up into two molecules of aniline. It is not basic; but, when treated with strong acids, it suffers molecular rearrangement, with formation of **benzidine**, or **p₍₂₎-diamido-diphenyl**, $\text{NH}_{2(4)}\text{.C}_6\text{H}_4\text{.C}_6\text{H}_4\text{.NH}_{2(4)}$.

The **unsymmetrical hydrazines** resemble each other in their properties and methods of formation, but differ from the symmetrical compounds, notably in that, containing the —NH.NH_2 group, they are monacid bases, forming salts corresponding to those of ammonia.

Phenylhydrazine — $\text{C}_6\text{H}_5\text{.NH.NH}_2$ — is formed by reduction of the diazo salts, of the diazo-amido compounds, or of the nitroso-amines. Thus stannous chloride and diazobenzene chloride yield phenylhydrazine hydrochloride:



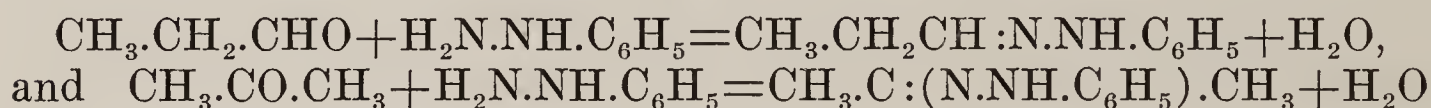
Zinc dust and acetic acid decompose diazoamido-benzene into phenylhydrazine and aniline:



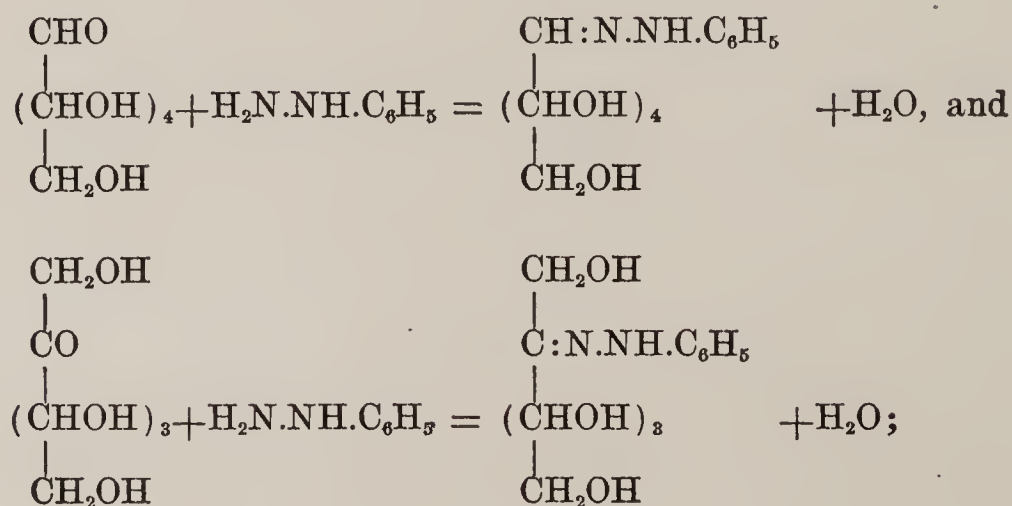
Phenylhydrazine is a yellow oil, which crystallizes at 23° , and boils at 242° with partial decomposition, or at 120° , without decomposition, under 12mm. pressure. It reduces Fehling's solution, or when boiled with CuSO_4 it liberates nitrogen and forms benzene. Sodium displaces the imide H to form α sodium phenylhydrazine: $\text{C}_6\text{H}_5\cdot\text{NaN}\cdot\text{NH}_2$. The alkyl halides cause substitution of alkyls for both amide and imide H, forming α and β phenylalkyl hydrazines. One of the latter, β methyl-phenylhydrazine, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_3$, is an intermediate product in the formation of antipyrine from phenylhydrazine. Heated to 200° with fuming HCl , phenylhydrazine is converted into p-phenylene-diamine: $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}_2 = \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$.

Phenyl-hydrazones and Osazones.—A most important action of phenylhydrazine is that with aldehydes and ketones, and with aldo- and keto-alcohols, and aldehyde and ketone acids and their esters, in which the bivalent remainder $=\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ takes the place of oxygen in the aldehyde or ketone group, with the formation of **phenyl-hydrazones** and **osazones**, in much the same manner as the aldoximes and ketoximes are formed from the aldehydes and ketones. The formation of these derivatives is utilized to identify the aldehydes and ketones and, notably, the aldoses and ketoses (p. 236, also "phenylhydrazine reaction").

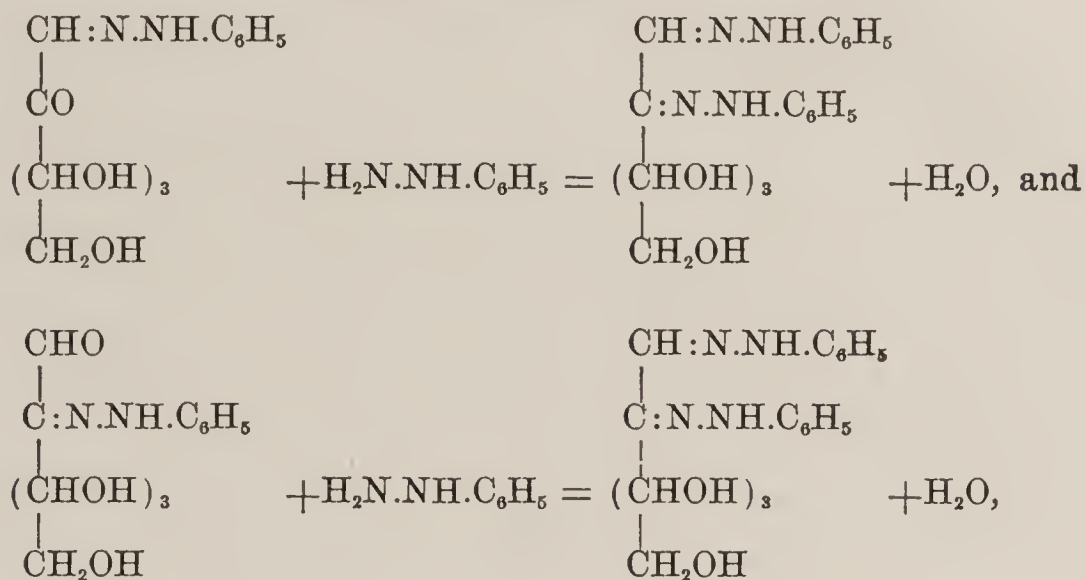
The phenyl-hydrazones and osazones are formed by a variety of methods, usually by heating the aldehyde or ketone compound with phenylhydrazine hydrochloride in presence of sodium acetate. In the formation of the **aldehydrazones** and **ketohydrazones** the reaction takes place with elimination of water according to the equations:



In the formation of the **osazones** of the aldoses and ketoses two molecules of phenylhydrazine react with one of the sugar, with elimination of water. In the first stage of the reaction a hydrazone is formed as with the aldehydes and ketones. Thus with glucose and fructose respectively (pp. 240, 241):



The CHOH or CH₂OH group vicinal to the first substitution then becomes oxidized to CO or CHO, and a second =N.NH.C₆H₅ group is substituted for the O to form the osazone:



A comparison of the above formulæ will indicate why it is that glucose and fructose yield one and the same osazone, called **glucosazone**.

The phenyl-hydrazones are also utilized in the formation of condensed heterocyclic compounds. Thus acetone phenyl hydrazone, $\text{CH}_3\text{C:N.NH.C}_6\text{H}_5$ is converted into a methyl indole (p. 415), $\text{CH}_3\text{C.NH}\begin{array}{l} \diagdown \\ \text{CH} \end{array}$ C_6H_4 , by loss of NH_3 .

Acid Derivatives of Phenylhydrazine.—A great number of compounds are known, formed by the substitution of acid radicals for the amide or imide hydrogen of phenylhydrazine. These compounds bear the same relation to phenylhydrazine that the anilides bear to aniline, and some of them have been used as antipyretics, *e. g.*, β **acetophenyl-hydrazide—Hydracetine**— $\text{C}_6\text{H}_5\text{.NH.NH.CO.CH}_3$ —formed as a white, crystalline, tasteless, and odorless powder, sparingly soluble in water, by the action of acetyl chloride or of acetic anhydride upon phenylhydrazine. It is the active ingredient of an antipyretic called **pyrodine**.

B. HYDROAROMATIC COMPOUNDS WITH A SINGLE NUCLEUS.

The hydroaromatic compounds may be considered as derived from the benzenic by rupture of one or more of the double linkages of the benzene ring (p. 336), by which the valence of the nucleus is changed from six to eight, ten or twelve.

HYDROCARBONS.

Hexahydrobenzenes—Cyclohexanes—Naphthenes.—These compounds, of which **hexahydrobenzene**, $\text{H}_2\text{C}\begin{array}{c} \diagup \text{CH}_2\text{CH}_2 \diagdown \\ \diagdown \text{CH}_2\text{CH}_2 \diagup \end{array} \text{CH}_2$, is the simplest, and the parent substance of the hydroaromatic compounds, exist in Russian petroleum, in coal tar, and in “rosin-oils.” They are isomeric with the olefines, from which they

may be distinguished by the fact that they do not combine with bromine. With chlorine they form mono-chlor substitution products which behave like alkyl chlorides.

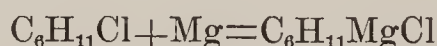
Terpenes.—Most of the volatile, or essential oils, or essences, obtained by distillation of various plants with steam, consist of hydrocarbons having the formula $C_{10}H_{16}$, and most of the camphors and resins are alcoholic or ketonic derivatives of these hydrocarbons. A few of the essential oils, having the formula C_5H_8 , are known as **hemiterpenes**, or **olefine terpenes**, and are unsaturated aliphatic compounds. Some of the aromatic terpenes also are polymers, having the formulæ $x(C_5H_8)$. Although the constitution of the aromatic terpenes is not completely established, they are hydro-aromatic hydrocarbons of which the camphors are alcohols or ketones.

Turpentine is a yellowish-white, semi-solid substance, having a balsamic odor, which exudes from incisions in the bark of *Pinus palustris*, *P. tæda*, and other *Coniferae*, and which may be taken as the type of a number of other similar products. These substances, when distilled with steam, yield two products, one a solid, yellow or brown residue, a **stearoptene**, such as **rosin** or **colophany**; the other a volatile, oily liquid, an **eleoptene**, such as **oil**, or **essence**, of **turpentine**. Oil of turpentine is insoluble in water, mixes with alcohol and with ether, and dissolves phosphorus, sulphur and caoutchouc. When exposed to the air it is oxidized to gummy, aldehydal products, which finally harden, hence its use as a drier in the manufacture of paints and varnishes. On contact with HNO_3 , its oxidation is so violent as to cause ignition.

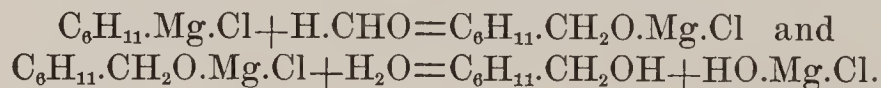
Hydroterpenes are naphthenes (p. 381) obtained by decomposition of certain natural alcohol-camphors. Thus **hexahydrocymene**, $H_3C.CH \begin{smallmatrix} \diagup CH_2.CH_2 \\ \diagdown CH_2.CH_2 \end{smallmatrix}$ $CH.CH \begin{smallmatrix} \diagup CH_3 \\ \diagdown CH_3 \end{smallmatrix}$, is derived from menthol (p. 383).

HYDROAROMATIC ALCOHOLS.

The **hydroaromatic alcohols** are, for the most part, "ring alcohols," and contain either $CHOH$ or COH , as a part of the ring, although in some, as in some of the terpan alcohols, the alcoholic group, which may then also be CH_2OH , is contained in the lateral chain. These alcohols may be obtained by reduction of the corresponding ketones, or of other aromatic or hydroaromatic compounds. They are produced by the action of organic magnesium compounds by reactions similar to those by which aliphatic alcohols are formed (p. 212). Magnesium cyclohexane chlorides are obtained by the action of magnesium upon cyclohexane chlorides:



and these in turn react with aldehydes and ketones to produce crystalline compounds from which the alcohols are produced by hydrolysis. Thus cyclohexyl carbinol is produced from hexahydrobenzene and trioxymethylene:



Several of them, such as quercite, inosite and some of the camphors, are natural products.

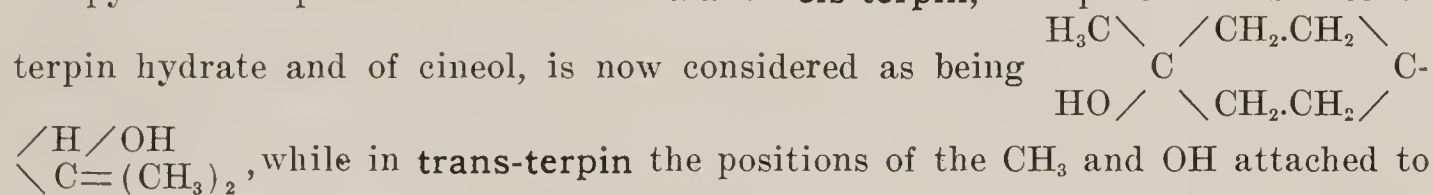
Quercite— $H_2C \begin{smallmatrix} \diagup CHOH.CHOH \\ \diagdown CHOH.CHOH \end{smallmatrix} CHO$ H—a pentatomic alcohol, obtained from acorns. It is a sugar-like substance, but is not affected by alkalies, does not ferment, and does not reduce Fehling's solution. F. p. 235° ; $[a]_D = +24.16^\circ$.

Inosite— $C_6H_6(OH)_6—CHOH \begin{smallmatrix} \diagup CHOH.CHOH \\ \diagdown CHOH.CHOH \end{smallmatrix} CHO$ H—metameric, though not related, to the glucoses, is a hexatomic alcohol, which exists in three optical modifications. The inactive modification exists in the liquid of muscular tissue,

in the lungs, kidneys, liver, spleen, brain and blood; in traces in normal urine, and increased in Bright's disease, in diabetes, and after the use of drastics in uremia; in the contents of hydatid cysts; in beans and peas, and in certain other seeds and leaves. It crystallizes in needles, usually arranged in cauliflower-like masses, has a sweet taste, is readily soluble in water, sparingly soluble in alcohol, insoluble in absolute alcohol and in ether. It does not ferment, is not colored by alkalies, and does not reduce Fehling's solution. When heated to 170° with HI, it is decomposed into phenol, diiodophenol and benzene. When treated with HNO₃ evaporated to near dryness, the residue moistened with NH₄OH and CaCl₂, and again evaporated, a rose-red residue is left (Scherer's reaction). Mercuric nitrate produces in solutions of inosite a yellow precipitate, which, on cautious heating, turns red. The color disappears on cooling and reappears on heating (Gallois' reaction).

Menthol—Oxyhexahydrocymene — $\text{H}_3\text{C}.\text{CH} \begin{array}{l} \diagup \text{CH}_2.\text{CH}(\text{OH}) \\ \diagdown \text{CH}_2.\text{CH}_2 \end{array} \text{CH}.\text{CH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$
—is a monacid menthan alcohol. It is the chief constituent of oil of peppermint. It crystallizes in prisms, fusible at 42°, sparingly soluble in water, readily soluble in alcohol, ether and carbon bisulphide, and in acids. Corresponding to it are a series of menthyl esters.

Terpins.—There are two diacid **menthan alcohols**, in which the hydroxyls occupy the 1.8 positions. The formula of **cis-terpin**, the parent substance of terpin hydrate and of cineol, is now considered as being



, while in **trans-terpin** the positions of the CH₃ and OH attached to C(1) are reversed. Cis-terpin is obtained by dehydration of terpin hydrate, and also from [d+1]-limonene dihydrochloride. It is crystalline, fuses at 104°, and boils at 258°. It absorbs water eagerly to form terpin hydrate. Gaseous HCl, or PCl₃, converts it into [d+1]-limonene hydrochloride.

Terpin Hydrate—C₁₀H₁₈(OH)₂+H₂O—is formed when oil of turpentine remains long in contact with water, more rapidly in presence of alcohol and dilute HNO₃; also, similarly, from pinene and from limonene. It forms rhombic crystals, fusible at 117°, with loss of H₂O and conversion, slowly, into terpin. It is easily soluble in alcohol, sparingly soluble in water, chloroform and ether. It is used as an expectorant.

Cineol—Eucalyptol—C₁₀H₁₈(OH)₂—another diacid menthan alcohol is obtained from the leaves of *Eucalyptus globulus*, and also exists in wormseed oil (*Oleum cinæ*) and in other volatile oils. It is a colorless oil, having a camphor-like odor; sp. gr. 0.93 at 15°; b. p. 176°; n_D = 1.4559; soluble in alcohol, sparingly soluble in water. Dry HCl gas passed through its petroleum ether solution separates white scales of **eucalypteol**, C₁₀H₁₆.2HCl, which is decomposed by water with regeneration of cineol.

Borneol—Camphol—Borneo Camphor—C₁₀H₁₈O—a monacid alcohol, is the best known of the **camphan alcohols**. It exists in three optical modifications; the **d-borneol** being the one usually met with, and obtained from *Dryobalanops camphora*. The d- and l-modifications are both formed by hydrogenation of laurel camphor. It forms small, friable crystals; has an odor recalling those of laurel camphor and of pepper, and a hot taste; is insoluble in water, readily soluble in alcohol, ether, and acetic acid; fuses at 203°; boils at 212°. It is oxidized to laurel camphor by HNO₃. Heated with KHSO₄, it is decomposed into camphene and H₂O.

HYDROAROMATIC KETONES AND ACIDS.

The **hydroaromatic ketones** are "ring ketones," the CO group forming a part of the ring. They are formed: (1) by reduction of the corresponding

aromatic phenols; (2) by oxidation of the secondary ring-alcohols: (3) by condensation of the esters of the aliphatic ketone acids, or of the ketones.

d-Camphor—**Common camphor**—**Laurel camphor**—**Japan camphor**— $C_{10}H_{16}O$ —is the most important of the hydroaromatic ketones. It is obtained from the camphor tree (*Laurus camphora*), and is formed artificially by oxidation of borneol or of camphene. It forms translucent, friable crystals; hot and bitter in taste, aromatic; sparingly soluble in water, quite soluble in acetic acid, methylic and ethylic alcohols, and the oils; f. p. 175° ; b. p. 204° ; sp. gr. 0.985; sublimes at all temperatures; $[a]_D = +44.22$.

It ignites readily, and burns with a luminous flame. Cold HNO_3 dissolves it, and H_2O precipitates it unchanged from the solution. Hot HNO_3 , or potassium permanganate, oxidizes it to d-camphoric acid. Distilled with P_2O_5 it yields cymene, $C_{10}H_{14}$. Reducing agents convert it into borneol. Heated with iodine, it is converted into carvacrol. Bromine unites with it to form ruby-red crystals of an unstable compound, $C_{10}H_{14}OBr_2$, which, when heated, fuse and give off HBr , leaving an amber-colored residue, which, on recrystallization from boiling alcohol, leaves long, hard, rectangular crystals of **monobromo-camphor**, $C_{10}H_{15}OBr$; f. p. 76° ; soluble in alcohol and in ether.

l-Camphor is obtained from the oil of *Matricaria postlanium*; $[a]_D = -44.22^{\circ}$. **[d+l]-Camphor** exists in the essential oils of rosemary, sage, lavender and origanum, or is formed by mixing d- and l- camphors, or by oxidation of [d+l]-borneol, or of [d+l]-camphene. F. p. 179° .

Hydroaromatic Carboxylic Acids.—A great number of these acids are known, some pure acids, others oxy- or ketonic acids, containing from one to six carboxyl groups, and hexahydro-, tetrahydro- and dihydro-. The most important are:

Quinic Acid—**Hexahydro-tetraoxybenzoic Acid**— $C_6H_7(OH)_4COOH$ —which exists, combined with the alkaloids, in cinchona barks, also in coffee beans and in other plants. It forms hard, transparent prisms, soluble in water and in alcohol; fuses at 160° ; laevogyrous. On distillation, it yields phenol, hydroquinol, benzoic acid and salicylic aldehyde. Hydriodic acid reduces it to benzoic acid.

Terebic Acid— $C_7H_{10}O_4$ —f. p. 175° ; and **Terpenylic Acid**— $C_8H_{12}O_4$ —f. p. 90° , are oxidation products of oil of turpentine, obtained, the former with HNO_3 , the latter with chromic acid mixture.

Camphoric Acids— $C_{10}H_{14}(COOH)_2$.—The d-, l-, and [d+l]-acids are known. **d-Camphoric acid** is produced by oxidizing common d-camphor by heating with HNO_3 . It forms colorless, odorless needles, soluble in alcohol, ether and boiling water; f. p. 187° ; $[a]_D = +49.7^{\circ}$. By further oxidation it yields camphoronic acid, or trimethyl-tricarballic acid.

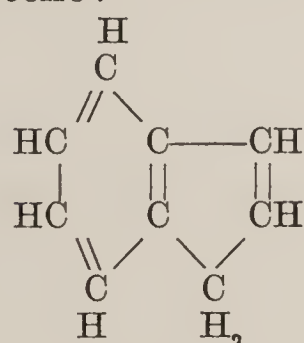
Resins—are generally the products of oxidation of the hydrocarbons allied to pinene; are amorphous (rarely crystalline); insol-

uble in water; soluble in alcohol, ether, and essences. Many of them contain acids.

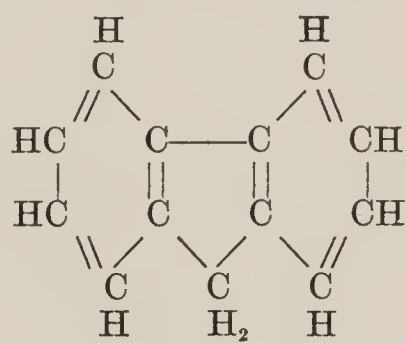
They may be divided into several groups, according to the nature of their constituents: (1) **Balsams**, which are usually soft or liquid, and are distinguished by containing free cinnamic or benzoic acid, *e.g.*, *benzoin*, *liquidambar*, *Peru balsam*, *styrax*, *balsam tolu*; (2) **oleo-resins** consist of a true resin mixed with an oil, *e.g.*, *Burgundy* and *Canada pitch*, *Mecca balsam*, and the resins of *capsicum*, *copaiba*, *cubebs*, *elemi*, *lupulin*; (3) **gum-resins**, mixtures of true resins and gums, *e.g.*, *aloes*, *ammoniac*, *asafetida*, *euphorbium*, *galbanum*, *guaiac*, *myrrh*, *olibanum*, *scammony*; (4) **true resins**, hard substances containing neither essences, gums nor aromatic acids, *e.g.*, *resin*, *copal*, *dammar*, *jalap*, *lac*, *sandarac*; (5) **fossil resins**, *e.g.*, *amber*, *asphalt*, *ozocerite*.

C. COMPOUNDS WITH CONDENSED NUCLEI.

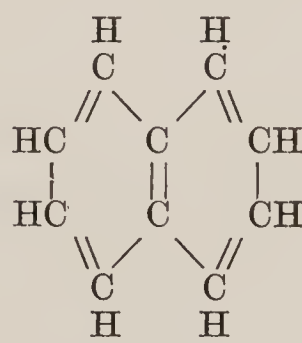
These compounds contain two or more benzene rings, or one or more benzene rings and a pentacarbo-cyclic ring, fused together in such manner that the adjacent rings have two carbon atoms in common. The parent hydrocarbons of these compounds are: indene, fluorene, naphthalene, anthracene, phenanthrene, chrysene, and picene:



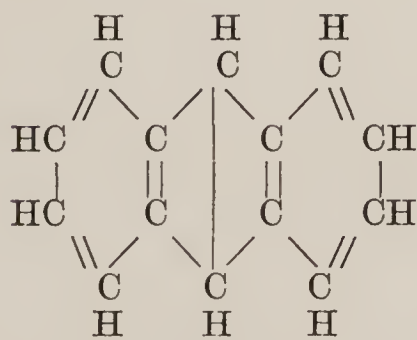
Indene.



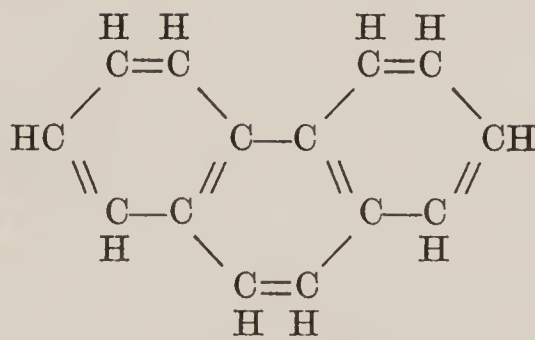
Fluorene.



Naphthalene.



Anthracene.



Phenanthrene.

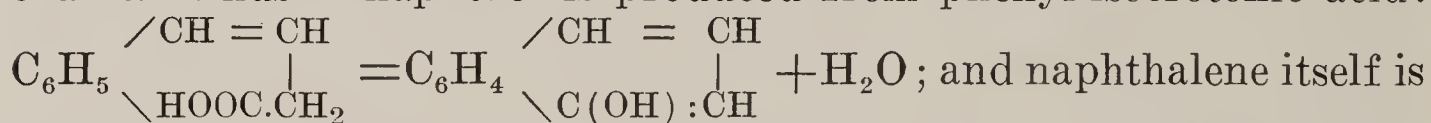
The derivatives of these hydrocarbons are similar in their general properties to the benzene derivatives, with some differences in orientation. Chrysene, $C_{18}H_{12}$, and picene, $C_{22}H_{14}$, are naphthalene-phenanthrenes. Most of these hydrocarbons form crystalline addition products with picric acid.

CONDENSED HYDROCARBONS.

These hydrocarbons accompany benzene in coal-tar. Naphthalene and anthracene are obtained from this source industrially.

Naphthalene— $C_{10}H_8$ —is obtained commercially from the fraction of coal-tar distillation passing between 180° and 300° . It crystallizes in shining plates; f. p. 79° ; b. p. 218° ; volatile at all temperatures, giving off a peculiar, tarry odor (white tar, moth-balls); sparingly soluble in cold alcohol, readily soluble in hot alcohol, ether and benzene. It is used in the arts in the preparation of phthalic acid and its derivatives, of the naphthols, etc., and of a great number of naphthalene dyes, for the carburation of water-gas, and against moths. Its picric acid compound fuses at 149° .

Naphthalene is undoubtedly formed in the distillation of coal by condensation of lower hydrocarbons under the influence of heat, a formation which may be imitated by conducting a mixture of benzene vapor with acetylene, or with ethylene, through a tube heated to redness. Naphthalene derivatives are also formed by condensation of several monobenzenic derivatives with unsaturated lateral chains. Thus α naphthol is produced from phenyl-isocrotonic acid:



formed when phenylbutylene vapor is passed over heated lime:

$$C_6H_5.CH_2.CH_2.CH:CH_2 = C_6H_4 \begin{array}{c} \diagup CH=CH \\ | \\ \diagdown CH=CH \end{array} + 2H_2.$$

Hydronaphthalenes and their substitution products are derived from naphthalene by rupture of one or more of the double bonds, in the same manner as the hydroaromatic compounds are derived from benzene.

Anthracene— $C_{14}H_{10}$ —is obtained commercially from the “green oil” of coal-tar, distilling above 270° ; and is used in the manufacture of alizarin dyes (artificial madder). It is formed from benzene and acetylene, or methylene bromide, in presence of $AlCl_3$. It crystallizes in colorless plates, having a fine blue fluorescence; f. p. 213° ; b. p. 351° ; sparingly soluble in benzene and in carbon bisulphide, which are its best solvents. Oxidizing agents convert it into anthraquinone. Its picric acid compound forms red needles, f. p. 138° .

PHENOLS, QUINONES.

The phenols, particularly those of naphthalene, the **oxynaphthalenes**, or **naphthols**, are the most important of those compounds. The naphthols exist in coal-tar, and are also manufactured synthetically by the methods indicated below. They readily form ethers, and with ammonia they produce the corresponding naphthylamines. Both naphthols are used medicinally as antiseptics.

α -Naphthol— $C_{10}H_7(OH)_\alpha$ —is obtained by heating phenyl isocrotonic acid; also by boiling an aqueous solution of diazonaphthalene nitrate with nitrous acid, or by fusing α -naphthalene-sulphonic acid with KOH.

It crystallizes in colorless prisms; f. p. 95° ; b. p. 280° ; nearly insoluble in water, soluble in alcohol and in ether; is easily volatile, and has the odor of phenol. It gives a transient violet color with $FeCl_3$ and a hypochlorite. With nitrous acid it forms, 2, 1 and 4, 1 **nitroso-naphthols**. Potassium chlorate and hydrochloric acid oxidize it to dichloro-naphthaquinone. Nascent hydrogen (sodium and alcohol) reduce it to **ar-tetrahydronaphthol** (below). Its acetate fuses at 46° .

β -Naphthol— $C_{10}H_7(OH)_\beta$ —is prepared industrially by fusion of sodium β -naphthalene-sulphonates with NaOH, for use in the manufacture of a number of dyes, among which are **Campobello yellow** and the **tropeolins**. It crystallizes in colorless, silky plates, which turn dark in daylight; has a faint phenol-like odor, and a sharp, burning taste; f. p. 123° ; b. p. 286° ; sparingly soluble in water, readily soluble in alcohol and in ether. It gives a greenish color with $FeCl_3$. Its acetate fuses at 70° .

Substituted Naphthols.—Both naphthols form a great number of derivatives by substitution of other groups for hydrogen atoms. Many of these are important dyes. Thus **Martius yellow** is the Na salt of 2, 4-dinitro- α -naphthol, a poisonous pigment sometimes used to color butter and confectionery. **Naphthol yellow** is the dipotassium salt of dinitro- α -naphthol-8-sulphonic acid. The naphthols combine easily with the diazo- and azo-compounds to form a number of **azo-naphthol** derivatives, several of which are important dyes, as the **naphthol oranges** and **Bieberich scarlet**. A great variety of **naphthol-sulphonic acids** have also been prepared for use in the color industry, as in the preparation of the various **ponceau** and **Bordeaux** dyes. These sulphonic acids, being basic by their OH group and acid by the HSO_3 group, form lactone-like compounds, which are called **sultones**.

Tetrahydronaphthols are formed by the introduction of four H atoms into one of the benzene rings, by the action of nascent hydrogen upon the naphthols. If the hydrogenation occur in the ring containing the OH, one product is obtained, designated by the prefix **ac-**, whereas if it occur in the other ring a different substance is produced, designated by the prefix **ar-**.

Quinones.—Naphthalene, anthracene and phenanthrene readily yield quinones, some of which are technically prepared by oxidizing the hydrocarbons in acetic acid solution by chromic acid; or from the dioxy- or diamido-compounds.

Naphthoquinones.—Oxidation of naphthalene produces α naphthoquinone, $C_{10}H_6:O_2$ (1, 4), which crystallizes in yellow needles, fusible at 125° . The α - β quinone, $C_{10}H_6:O_2$ (1, 2), is formed by oxidation of β amido- α -naphthol, and crystallizes in red needles, fusible at 115° . Both naphthoquinones form oximes and hydrazones, some of which are used in the color industry.

Anthraquinone—Diphenylene Diketone— $C_6H_4(CO)_2:C_6H_4$ —is commercially manufactured by oxidation of anthracene. It forms yellow needles; f. p. 285° ; b. p. 382° . It forms an oxime with hydroxylamine, and sulphonic acids with H_2SO_4 , as well as chlorine, bromine and oxy-derivatives.

Alizarin — 1, 2-Dioxyanthraquinone — $C_6H_4:(CO)_2:C_6H_2:(OH)_2$ — is prepared industrially by the action of fused NaOH upon anthraquinone-monosulphonic acid, and is also formed by fusion of several other anthraquinone derivatives with caustic alkalies. It is the coloring principle of madder (*Rubia tinctoria*), and the artificial product has now completely displaced madder in dyeing.

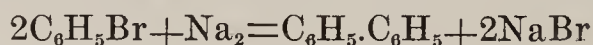
Purpurin — 1, 2, 4-Trioxanthraquinone — $C_6H_4:(CO)_2:C_6H:(OH)_3$ — is another constituent of madder, also obtained artificially by oxidation of alizarin, or from tribromo-anthraquinone.

Both alizarin and purpurin form nitro- and amido- substitution products which are also used as dyes; alizarin orange, blue and brown.

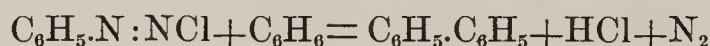
D. DIPHENYL AND ITS DERIVATIVES.

Diphenyl, $C_6H_5.C_6H_5$, is the type of the hydrocarbons, known as **phenylbenzenes**, formed by the substitution of phenyl, toluyl, benzyl, etc., for atoms of hydrogen in benzene (see formula of p₂-diamido-diphenyl, p. 340). Thus we have, besides diphenyl, **toluyl-benzene**, $C_6H_5.C_6H_4.CH_3$, **diphenyl-benzene**, $C_6H_4:(C_6H_5)_2$, and **triphenyl-benzene**, $C_6H_3:(C_6H_5)_3$. These hydrocarbons are the parent substances of a great number of substitution products. The mono-substituted compounds are o-, m-, or p-, with reference to the point of union of the benzene rings. In the bi- and polysubstituted derivatives the substituents may be introduced into the same or into different rings. Bi-substitution of bivalent groups for H₂ in the o-o₂-positions produces compounds belonging to other series of our classification.

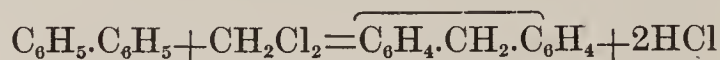
Diphenyl—Phenylbenzene — $C_6H_5.C_6H_5$ — exists in small quantity in gas-tar. It is formed by the action of sodium upon monobromo-benzene:



Or by passing benzene vapor through a red-hot tube; or by the interaction of diazobenzene chloride and benzene in presence of aluminium chloride:



It crystallizes in large plates; f.p. 70°; b.p. 254°; soluble in glacial acetic acid and in amyl alcohol. Nascent hydrogen converts it into **tetrahydro-diphenyl**, $C_{12}H_{14}$. With methylene chloride, in presence of AlCl₃ it forms fluorene:



E. DIPHENYL-PARAFFINS, DIPHENYL-OLEFINES, DIPHENYL-ACETYLENES.

The hydrocarbons of this series may be considered as derived from the aliphatic hydrocarbons by substitution of two (or more) phenyl groups for hydrogen:

$C_6H_5.CH_3$ — Phenyl-methane = Toluene = Methyl-benzene (p. 342).

$C_6H_5.CH_2.C_6H_5$ — Diphenyl-methane = Benzyl-benzene (formula p. 340).

$(C_6H_5)_2:CH.C_6H_5$ — Triphenyl-methane.

$(C_6H_5)_2:Si:(C_6H_5)_2$ — Tetraphenyl-silicon (C compound unknown).

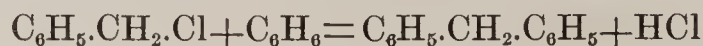
$C_6H_5.CH_2.CH_2.C_6H_5$ — Sym. Diphenyl-ethane = Dibenzyl.

$(C_6H_5)_2:CH.CH_3$ — Unsym. Diphenyl-ethane.

$C_6H_5.CH:CH.C_6H_5$ — Sym. Diphenyl-ethylene = Stilbene.

$C_6H_5.C \equiv$ Diphenyl-acetylene = Tolane.

Diphenyl-methane—Benzyl-benzene — is produced by the action of benzyl chloride upon benzene in presence of aluminium chloride:



It is a crystalline solid; f. p. 27° ; b. p. 262° ; soluble in alcohol, ether, and chloroform; has an odor resembling that of the orange.

Triphenyl-methane—is formed by the action of chloroform upon benzene in presence of aluminium chloride:



It is a crystalline solid; f. p. 92° ; b. p. 360° ; soluble in ether and in chloroform. It is converted into a trinitro-derivative by fuming HNO_3 ; and this, in turn, is converted by nascent H into leuco-pararosanilin, $\text{CH}(\text{C}_6\text{H}_4.\text{NH}_2)_3$.

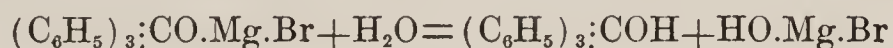
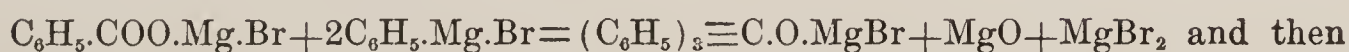
Stilbene—Toluylene—Sym. Diphenyl-ethylene—is formed by distillation of benzyl sulphide; by reduction of benzoic aldehyde; or by distillation of the phenylic esters of fumaric or cinnamic acids. It forms large, glistening prisms or plates; f. p. 124° ; b. p. 306° . It forms a number of haloid and other derivatives.

PHENOLS AND ALCOHOLS.

Phenolic derivatives of these hydrocarbons are known, which contain hydroxyls in one or more of the phenyl groups.

Diphenyl Carbinol—Benzhydrol— $\text{C}_6\text{H}_5.\text{CHOH.C}_6\text{H}_5$ —is the simplest alcohol of this series. It is formed in colorless crystals; f. p. 68° ; b. p. 298° ; by reduction of benzophenone with sodium amalgam, $\text{C}_6\text{H}_5.\text{CO.C}_6\text{H}_5 + \text{H}_2 = \text{C}_6\text{H}_5.\text{CHOH.C}_6\text{H}_5$.

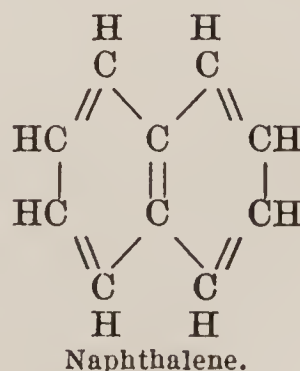
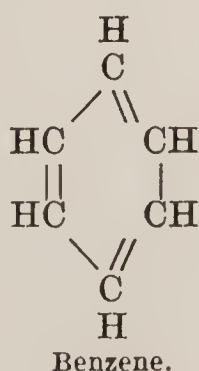
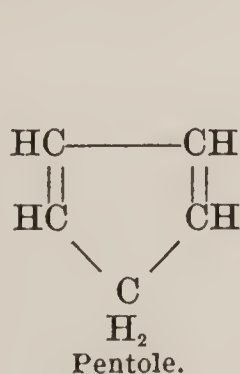
Triphenyl Carbinol, $(\text{C}_6\text{H}_5)_3\text{C.OH}$, and **diphenyl-m-toluy carbinol**, $(\text{C}_6\text{H}_5)_2\text{:C(OH).C}_6\text{H}_4.\text{CH}_3$ (3), are alcohols, whose triamido-derivatives are pararosanilin and rosanilin. They are formed by oxidation of the hydrocarbons. Triphenyl carbinol is the principal product of the action of CO_2 on phenyl magnesium bromide. In the first stage of the reaction:

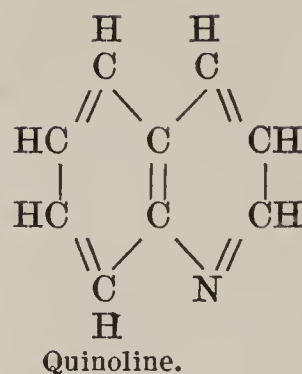
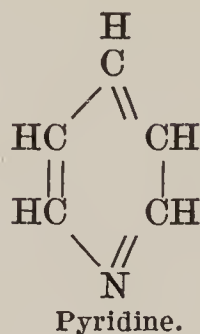
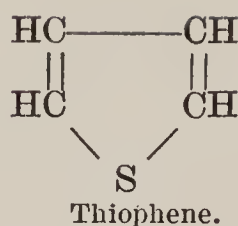


These reactions are somewhat similar to those by which tertiary aliphatic alcohols are produced by acidyl halides and oxides (see No. 10, p. 213). They form nitro- and amido-derivatives of technical importance.

HETEROCYCLIC COMPOUNDS.

These compounds differ from the carbocyclic in that they contain elements other than carbon as constituents of the nuclei. They form series parallel to the carbocyclic, from which, indeed, they may be considered as being derived by substitution in the rings. Thus thiophene corresponds to pentole, pyridine to benzene, and quinoline to naphthalene:

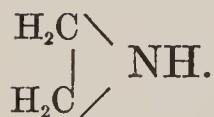




The elements which can be thus introduced into a cyclic nucleus are few; oxygen, sulphur, selenium, phosphorus and nitrogen being the only ones now known to enter into such formation, and of these the nitrogen-containing compounds are far the most numerous and the most important. The facility with which the N atom takes the place of the methine group, —CH= , in the benzene ring is to be anticipated from their equivalence. Pyridine also resembles benzene in its general characters, and, on the other hand, the five membered compounds, furfuran, thiophene and pyrrole, have general characters similar to those of benzene, from which they may be considered as being derived by substitution of the bivalents O, S, and NH for one of the three acetylenes, —CH:CH— , of benzene. The number of hetero-atoms which may be contained in the nucleus is not limited to one, and five and six membered rings containing as many as four nitrogen atoms, the tetrazoles and tetrazines, are known.

A classification of the heterocyclic compounds requires many subdivisions, because of the great number and variety of these substances, due to the presence of one or more atoms of one or more of the elements above mentioned, in three, four, five or six membered rings, contained in mono-, di-, tri-, or tetra-nucleate molecules, in which, also, differences in the ring-valence are caused by differences in internal linkage. A broad classification may, however, be here followed, somewhat similar to that for the aromatic substances (p. 339).

A. Mono-nucleate compounds: containing a single nucleus. These may be subdivided into : (a) Substances containing three-membered rings; such as ethylene oxide, $\begin{array}{c} \text{H}_2\text{C} \backslash \\ | \\ \text{H}_2\text{C} / \end{array} \text{O}$, sulphide, $\begin{array}{c} \text{H}_2\text{C} \backslash \\ | \\ \text{H}_2\text{C} / \end{array} \text{S}$, and imide,



(b) Four-membered compounds, such as trimethylene oxide, $\begin{array}{c} \text{H}_2\text{C}-\text{O} \\ | \quad | \\ \text{H}_2\text{C}-\text{CH}_2 \end{array}$, thetin, $\begin{array}{c} \text{H}_2\text{C}-\text{O} \\ | \quad | \\ \text{H}_2\text{C}-\text{S} \end{array}$, and trimethylene imide, $\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ | \quad | \\ \text{H}_2\text{C}-\text{NH} \end{array}$

(c) Five-membered substances, such as furfuran, $\begin{array}{c} \text{HC}=\text{CH} \backslash \\ | \\ \text{HC}=\text{CH} / \end{array} \text{O}$, thiophene, $\begin{array}{c} \text{HC}=\text{CH} \backslash \\ | \\ \text{HC}=\text{CH} / \end{array} \text{S}$, and pyrrole, $\begin{array}{c} \text{HC}=\text{CH} \backslash \\ | \\ \text{HC}=\text{CH} / \end{array} \text{NH}.$

(d) Six-membered compounds, such as pyridine, $\begin{array}{c} \text{HC}-\text{CH}=\text{CH} \\ || \\ \text{HC}-\text{CH}=\text{N} \end{array}$
 piperidine, $\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2 \\ | \qquad \qquad | \\ \text{H}_2\text{C}-\text{CH}_2-\text{NH} \end{array}$, and sym. tetrazine, $\begin{array}{c} \text{N}=\text{N}-\text{CH} \\ | \qquad \qquad || \\ \text{HC}=\text{N}-\text{N} \end{array}$

The five- and six-membered compounds are much more numerous and important than the three- and four-membered.

B. Condensed compounds, containing two or more rings, usually five- or six-membered, of which at least one is heterocyclic, fused together, and having two carbon atoms in common. These compounds, which correspond to the condensed benzenic compounds (p. 385), include the indole, quinoline, authraquinoline, quinquino-line, and diphenylene derivatives.

C. Compounds containing two (or more) nuclei, one at least heterocyclic, united directly without fusion, corresponding to the diphenyls, and including phenyl-pyridyl, dipyridyl, pyridyl-pyrrole, and pyridyl-piperidyl derivatives.

D. Compounds containing two (or more) nuclei, one at least heterocyclic, united by aliphatic groups, corresponding to the diphenyl-paraffins, and including the "ester-alkaloids" such as atropine, cocaine, etc.

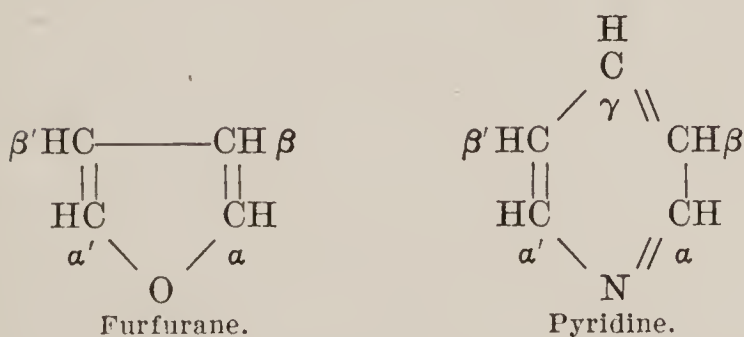
In a more detailed classification the members of the several classes are subdivided into the groups, of **mono-**, **di-**, **tri-**, and **tetrahetero-atomic compounds**, according as they contain one, two, three or four atoms other than carbon, of like or different kinds, in the ring.

A.—MONONUCLEATE HETEROCYCLIC COMPOUNDS.

FIVE MEMBERED RINGS.

The parent substances of these compounds are furfurane, thiophene, and pyrrole (see p. 390).

The heterocyclic rings differ from the carbocyclic in that the several carbon atoms are not equal in value, and therefore two different monosubstituted derivatives exist for the five-membered rings containing a single hetero-atom, such as furfurane, and three such compounds in six-membered rings, such as pyridine, according to the position of substitution with reference



to the hetero-atom. These positions are distinguished by the first three letters of the Greek alphabet, as shown in the margin, or, sometimes by numbers. The positions α and α' , and β and β' are of equal value.

Furfurane— $\begin{array}{c} \text{HC}=\text{CH} \backslash \\ | \\ \text{HC}=\text{CH} / \end{array} \text{O}$ —exists in the product of distillation of pine and fir wood, and is also formed by distillation of barium pyromucate (below), and from **dihydrofurfurane**, $\begin{array}{c} \text{HC}-\text{CH}_2 \backslash \\ | \\ \text{HC}-\text{CH}_2 / \end{array} \text{O}$, a product of reduction of erythrol (p. 224). It is a liquid; b. p. 32° ; having a peculiar odor. Its vapor colors a pine shaving moistened with HCl green (pp. 346, 393).

α -Furfuraldehyde—Furfurole—Furfural—Furole— $\begin{array}{c} \text{HC}=\text{C}-\text{CHO} \\ | \quad \backslash \\ \text{HC}=\text{CH}-\text{O} \end{array}$ —is produced by the dry distillation of sugar or of wood; by the distillation of these substances, or of bran, carbohydrates or glucosides with dilute H_2SO_4 ; by the action of the concentrated acid upon carbohydrates; and by distilling pentoses (p. 247), or glucuronic acid (p. 266) with HCl. It is a colorless liquid; agreeable in odor; b. p. 162° ; soluble in water and in alcohol. Being an aldehyde, it undergoes the reactions common to those substances. In concentrated solution, with urea and a trace of acid, it is colored yellow, changing to blue, to violet and to purple, and finally fading, with formation of a black precipitate (Schiff's reaction). It produces a red color with aniline, a very sensitive reaction for its presence. Paper moistened with aniline acetic solution is used. Pettenkofer's reaction for the biliary salts, etc., depends upon the formation of furfurole.

α -Furfurane Carboxylic Acid—Pyromucic acid— $\begin{array}{c} \text{HC}=\text{C}-\text{COOH} \\ | \quad \backslash \\ \text{HC}=\text{CH}-\text{O} \end{array}$ —the acid corresponding to furfurole, is produced from that substance by oxidation, also by distillation of mucic and isosaccharic acids (p. 265). It is a solid; f. p. 134° .

Thiophene— $\begin{array}{c} \text{HC}=\text{CH} \backslash \\ | \\ \text{HC}=\text{CH} / \end{array} \text{S}$ —and its superior homologues, methylthiophenes, etc., occur in gas-tar, and accompany the various products, benzene, etc., obtained from it. It is a colorless liquid; b. p. 84° ; which is so nearly that of benzene, 80.5° , that the two substances cannot be separated by distillation. With sulphuric acid and isatine it gives a fine color, due to formation of indophenine. Sulphuric acid alone is colored brown by thiophene, which it absorbs; and thiophene may be recovered from the solution by neutralization and distillation.

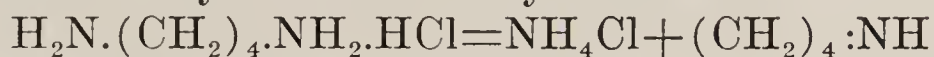
Pyrrole— $\begin{array}{c} \text{HC}=\text{CH} \backslash \\ | \\ \text{HC}=\text{CH} / \end{array} \text{NH}$ —exists in coal-tar and accompanies the pyridine bases (p. 397) in oil of Dippel. It is formed in a great variety of reactions, as by the action of baryta at 150° upon albumins, by the dry distillation of gelatin or of ammonium saccharate, etc. It is a colorless, oily liquid, having the odor of chloroform; b. p. 131° . Being a secondary amine, it has basic properties,

and its imide hydrogen is readily replaced by other atoms or groups. A pine shaving moistened with HCl is colored flame-red by pyrrole (the pine-shaving reaction; see also, Phenol, p. 346). It also yields an indigo-blue color with H_2SO_4 and isatine. Heated with dilute acids it gives off ammonia, and a red powder (pyrrole red) is deposited.

The homologous pyrroles, methyl-pyrroles, etc., have reactions similar to those of pyrrole.

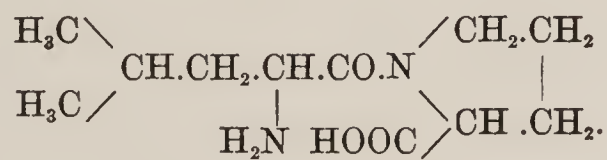
Hydropyrrole Derivatives—Nascent hydrogen combines with pyrrole to form, first dihydropyrrole, or pyrroline, $\begin{array}{c} \text{CH}:\text{CH} \backslash \\ | \quad \quad \text{NH} \\ \text{CH}_2.\text{CH}_2 / \end{array}$, an alkaline liquid, soluble in water; b. p. 91° ; and, finally, tetrahydropyrrole, or pyrrolidine, or tetramethylene-imine, $\begin{array}{c} \text{CH}_2.\text{CH}_2 \backslash \\ | \quad \quad \text{NH} \\ \text{CH}_2.\text{CH}_2 / \end{array}$,

which bears the same relation to pyrrole that piperidine does to pyridine (p. 398). Pyrrolidine resembles piperidine in its reactions, and also forms an addition product with methyl iodide. It is formed by heating tetramethylene-diamine hydrochloride:



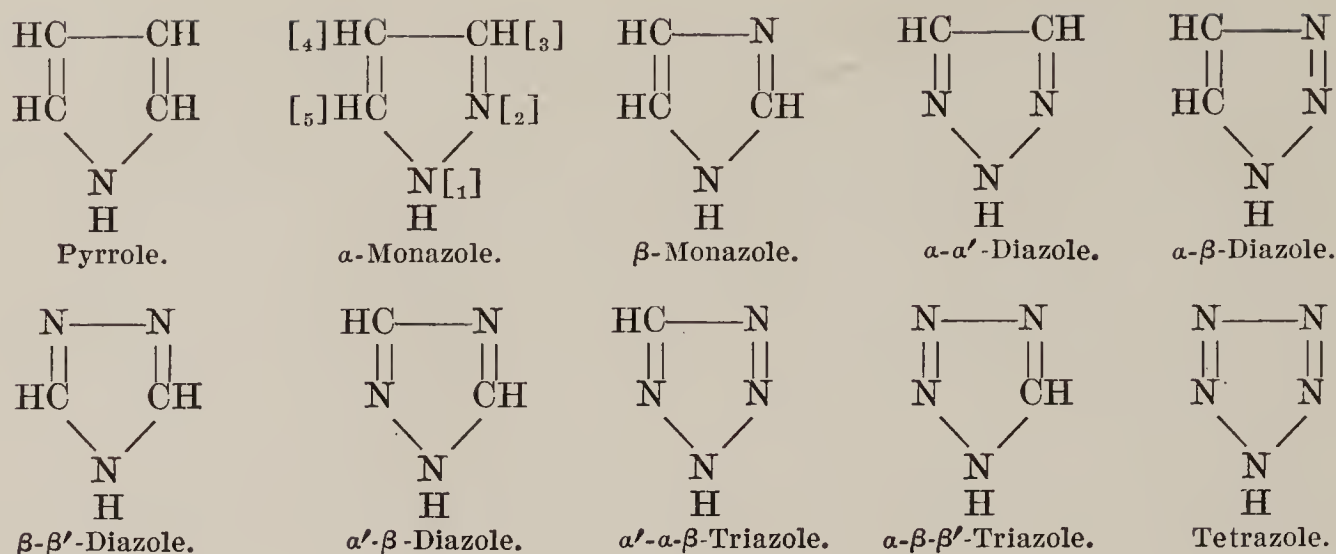
and constitutes the nucleus of the hygrines and one of those of nicotine. It is a strongly alkaline liquid; b. p. 87° . Among the derivatives of pyrrolidine is pyrrolidone, or butyrolactam, $\begin{array}{c} \text{CH}_2.\text{CH}_2 \backslash \\ | \quad \quad \text{NH} \\ \text{CH}_2.\text{CO} / \end{array}$, a simple cyclic imide derived from γ -amidobutyric acid.

α Pyrrolidine Carboxylic Acid—Proline—is a product of hydrolysis, by HCl or by tryptic digestion, of casein and gelatin, in which it probably exists as a dipeptide, constituted by substitution of the radical of α -amido-isocaproic acid for the imide hydrogen of the cyclic compounds:



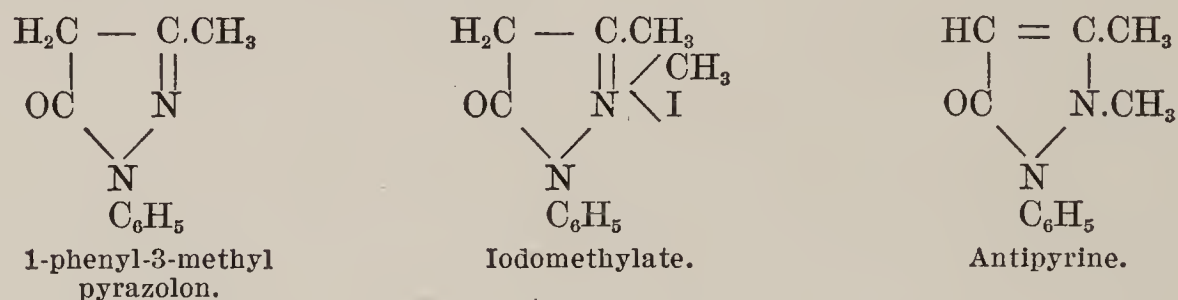
AZOLES AND THEIR DERIVATIVES.

The azoles are derivable from furfurane, thiophene and pyrrole by substitution of one or more N atoms for methine groups in the five-membered ring. They are distinguished, according to their parent substances, into furazoles, thioazoles, pyrroazoles and selenazoles, there being nine possible of each class, or they may be considered as derived from pyrrole by substitution of further hetero atoms in the ring. They are further distinguished as monazoles, diazoles, triazoles and tetrazoles, according to the number of introduced N atoms. Thus the formulæ of pyrrole and of the nine pyrroazoles are:



Corresponding to each of these compounds there are numerous derivatives, formed by substitution, or by modification of internal linkages and addition.

Antipyrine—1-Phenyl-2,3-dimethyl Pyrazolon—(formula below)—is formed, as its hydroiodide, by heating 1, 3-phenylmethyl pyrazolon, with methyl iodide and methylic alcohol to 100° in sealed vessels. In this reaction the I-pyrazolon type is maintained in the product of addition, but on splitting off HI to liberate the free base the antipyrine type is produced:

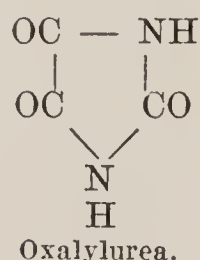
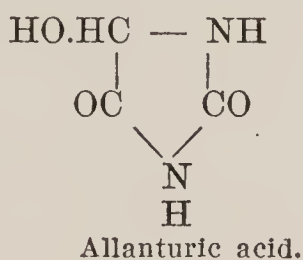
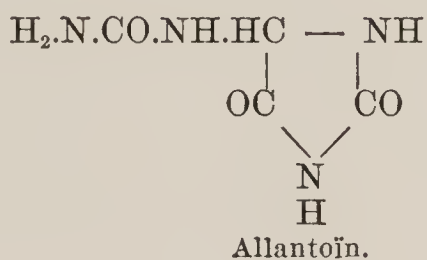
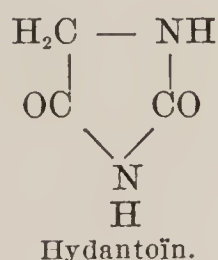


Antipyrine forms colorless, odorless scales, somewhat bitter in taste; f. p. 110.5°. A mixture of equal parts of antipyrine and anti-febrin (f. p. 112.5°) fuses at 45°. Antipyrine is readily soluble in water, alcohol and chloroform, less soluble in ether. With nitrous acid or the nitrites (sp. æth. nitr.), in the presence of free acid, it forms a green, crystalline, sparingly soluble nitro-derivative, which is poisonous. Its solution is colored deep red-brown by FeCl₃, the color being discharged by H₂SO₄. Nitrous acid colors its solutions bright green, and on heating the mixture, after addition of a drop of fuming nitric acid, the color changes to light-red, then to blood-red, and finally a purple oil is deposited. Addition of a drop of fuming nitric acid to cold, concentrated solution of antipyrine causes precipitation of small, green crystals. Antipyrine is strongly basic, and some of its salts are used in medicine: **Salipyrine** is antipyrine **salicylate**. It is formed by the action of the acid and the base upon each other at 100°. It is a white, crystalline powder, almost insoluble in water.

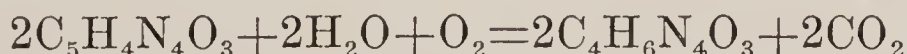
Tolypyrine—1-toluy- 2, 3-dimethyl pyrazolon—is obtained in the same manner as antipyrine, using p-toluy-hydrazine in place of phenyl-hydrazine and contains toluy, $C_6H_4.CH_3$ in place of phenyl. It forms colorless crystals; f. p. 136° ; and has a physiological action similar to that of antipyrine.

Hydantoin, — Glycolylurea — 2, 5-diketotetrahydroglyoxalin — (formula below) is the simplest of the cyclic monureides (p. 316), and is formed by the action of HI upon allantoin, or upon alloxanic acid. It is converted into the corresponding open chain compound, hydantoic, or glycoluric acid, $H_2N.CO.NH.CH_2.COOH$, by heating with $Ba(OH)_2$.

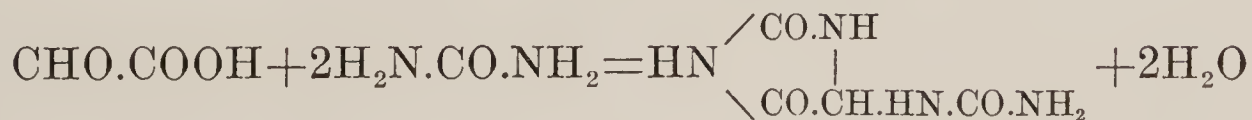
Corresponding to hydantoin are a number of substituted hydantoins, constituted by substitution of alkyls for H in the several positions. The β -compounds are formed by heating the monoalkyl amidoacids with urea. Thus urea and sarcosine yield β -methylhydantoin:



Allantoin, — Glyoxyldiureide — (formula above) — a derivative of hydantoin, occurs in the allantoinic fluid of the cow, in the urine of sucking calves, of dogs and cats fed on meat, of children during the first few days of life, of adults after administration of tannin, and of pregnant women; also in beet juice. It is also formed during autolysis of pancreas, liver and spleen. It is obtained by oxidation of uric acid by lead peroxide:



Or, synthetically from glyoxylic acid and urea:



It crystallizes in prisms, sparingly soluble in cold water, readily soluble in hot water and in alcohol. On reduction by HI it yields hydantoin and urea. Heated with alkalis it is decomposed into ammonia and carbonic, oxalic and acetic acids; glyoxylic acid being probably first formed and decomposed. Warmed with $Ba(OH)_2$, or with PbO_2 , it splits off urea and forms allanturic acid (formula above).

Oxalylurea, — Parabanic Acid — 2, 4, 5-triketotetrahydroglyoxalin — (formula above) is formed by oxidation of uric acid or of alloxan

by HNO_3 ; or synthetically by the action of POCl_3 or PCl_3 on a mixture of oxalic acid and urea:



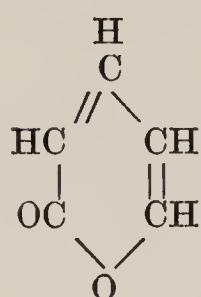
Its salts are converted into oxalurates by water.

Histidin— $\text{C}_6\text{H}_9\text{N}_3\text{O}_2$ —one of the hexon bases, is produced by hydrolysis of proteins. It crystallizes in rhombic plates or needles, is sparingly soluble in water, insoluble in alcohol and ether and is dextrorotary. It is only faintly alkaline, but expels CO_2 from Ag and Cu carbonates. By oxidation by KMnO_4 in alkaline solution it yields HCN , CO_2 and NH_3 , but it is not attacked by $\text{KMnO}_4 + \text{H}_2\text{SO}_4$. When boiled with $\text{Ba}(\text{OH})_2$ it does not give off NH_3 . It does not give the biuret reaction. It contains two H atoms replaceable by metals, and it forms two series of salts with acids. Nitrous acid separates one N atom as free nitrogen, and it forms one substitution product with β -naphthalene sulphonic acid; but two of its N atoms are capable of salt formation. It therefore contains one NH_2 and one NH , and the third N is tertiary. When heated it gives off CO_2 , and leaves a compound $\text{C}_5\text{H}_7\text{N}_2.\text{NH}_2$, and therefore it contains a COOH . The small proportion of H indicates a closed chain nucleus, and its reactions indicate two double linkages in the ring. It gives the Weidel reaction faintly. When diazobenzene-sulphonic acid ($\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{SO}_3\text{H}$, or sulphanilic acid and KNO_2 : the diazo reaction) is added to a solution of histidin in Na_2CO_3 , a coloring matter is formed which is orange in acid solution and dark cherry-red in alkaline solution. The only other product of protein hydrolysis which gives this reaction is tyrosin. Histidin is a derivative of glyoxaline, whose constitution

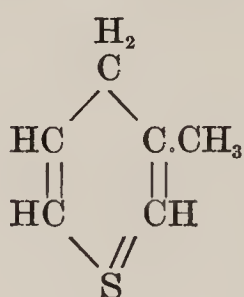
is probably $\text{N} \begin{array}{l} // \text{CH.NH} \\ | \\ \diagdown \text{CH:C.CH}_2.\text{CHNH}_2.\text{COOH} \end{array}$, β . glyoxaline α . amido-propionic acid.

SIX MEMBERED RINGS.

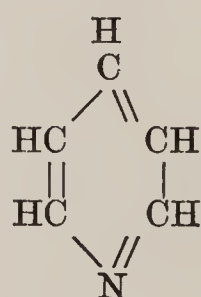
Six membered heterocyclic compounds are known, containing oxygen, sulphur and nitrogen in the nucleus:



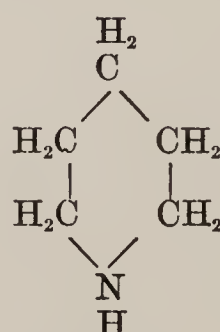
α -Pyrone.



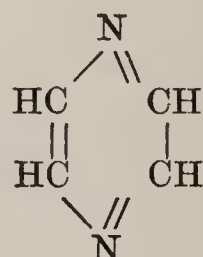
β -Methylpenthiophene.



Pyridine.



Piperidine.



Pyrazine.

The oxygen and sulphur compounds are neither numerous nor important. Some of the former are products of condensation of aliphatic compounds, δ -lactones and δ -anhydrides.

Pyrone (γ)—*Pyrocomane*— $\text{O} \begin{smallmatrix} \diagup \text{CH}=\text{CH} \diagdown \\ \diagdown \text{CH}=\text{CH} \diagup \end{smallmatrix} \text{CO}$ —is an oxidized derivative of γ furane, produced from comenic acid by the action of heat and constituting the nucleus of comenic, chelidonic, and meconic acids.

Comenic acid— $\text{C}_5\text{H}_2\text{O}_2(\text{OH}).\text{COOH}$ —is produced by the action of hot H_2O , of dilute acids, or of bromine water upon meconic acid. It crystallizes in yellowish prisms, rather soluble in H_2O . It is monobasic. It is decomposed by heat into CO_2 and pyrone.

Chelidonic acid— $\text{C}_5\text{H}_2\text{O}_2(\text{COOH})_2$ —exists in chelidonium, in combination with the alkaloids **sanguinarine** and **chelidonine**. It is a crystalline solid and a dibasic acid. Heat converts it into comenic acid, which in turn yields pyrone.

Meconic acid— $\text{C}_5\text{HO}_2(\text{OH})(\text{COOH})_2$ —is peculiar to opium, in which it exists in combination with a part, at least, of the alkaloids. It crystallizes in small prismatic needles; acid and astringent in taste; loses its Aq at 120° ; quite soluble in water, soluble in alcohol, sparingly soluble in ether.

With ferric chloride it forms a blood-red color, which is not discharged by dilute acids or by mercuric chloride; but is discharged by stannous chloride and by the alkaline hypochlorites.

PYRIDINE BASES AND THEIR DERIVATIVES.

The **pyridine bases**, closely related to the vegetable alkaloids (p. 419) as well as to some of the basic substances formed during putrefaction, were first obtained from **oil of Dippel**, or **bone-oil** (*Oleum animale*), an oil produced during the dry distillation of bones, horns, etc., and as a by-product in the manufacture of ammoniacal compounds from those sources. They also occur in coal-tar, naphtha, commercial ammonia, methylic spirit and fusel oil. They are formed synthetically: (1) By heating the aldehyde-ammonias alone, or with aldehydes or ketones; (2) From pyrrole by the action of K or Na in presence of methylene iodide, etc.; (3) By oxidation of hexahydropyridines, piperidines; also by other methods.

The pyridine bases are colorless liquids of peculiar, penetrating odor. The superior homologues are metamerie with the anilines. They are strong triacid bases, and behave like tertiary monamines. Oxidizing agents do not attack pyridine, nor the nucleus of its superior homologues, but the lateral chains of the picolines, etc., are readily oxidized, with formation of **carbopyridic acids**. Reducing agents convert them into **piperidines** (p. 398). They react with several of the general reagents for the alkaloids (p. 421). The two most nearly characteristic properties of the pyridine bases are: (1) the formation of chloroplatinates such as $(\text{C}_5\text{H}_5\text{N}.\text{HCl})_2\text{PtCl}_4$, which on boiling with water, lose two molecules of HCl to form "modified salts" such as $(\text{C}_5\text{H}_5\text{N})_2\text{PtCl}_4$ (Anderson's reaction), and, (2) the formation of crystalline addition products, **alkyl-pyridinium iodides**, such as $\text{C}_5\text{H}_5\text{N} \begin{smallmatrix} \diagup \text{CH}_3 \\ \diagdown \text{I} \end{smallmatrix}$ on contact of their alcoholic solutions with alkyl iodides.

Pyridine— $\text{HC} \begin{smallmatrix} \diagup \text{CH}:\text{CH} \diagdown \\ \diagdown \text{CH}.\text{CH} \diagup \end{smallmatrix} \text{N}$ —is obtained from oil of Dippel, or from piperidine. It boils at 115° , mixes with water in all proportions,

is strongly alkaline in reaction. Its hydrochloride is crystalline, but deliquescent. Its chloroplatinate fuses at 240° . When reduced by sodium and alcohol, it forms piperidine, or hexahydropyridine; and when reduced by hydriodic acid, normal pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

Pyridine Homologues—Alkyl Pyridines—are substitution products containing alkyl groups for H. Owing to the inequality in value of the several C atoms of pyridine (p. 397), the number of substituted derivatives is greater than with benzene. There are three monosubstituted derivatives, six each of the bi- and tri-substituted, three tetra-, and one penta-substituted.

Methyl-pyridines—Picolines— $\text{C}_5\text{H}_4\text{N}(\text{CH}_3)$ —The three picolines, α , β and γ , exist in oil of Dippel, and have been formed synthetically. Their b. p.'s are 130° , 143° , and 144° .

Lutidines—Three ethyl pyridines, $\text{C}_5\text{H}_4\text{N}(\text{C}_2\text{H}_5)$, are known, α , b. p. 148° , β , b. p. 166° ; and γ , b. p. 165° . Of the six possible dimethyl-pyridines, $\text{C}_5\text{H}_3\text{N}(\text{CH}_3)_2$, four are known, three of which exist in bone oil.

Collidines— $\text{C}_8\text{H}_{11}\text{N}$ —There are twenty-two possible collidines, of which twelve are known. Of these several are products of decomposition of vegetable alkaloids, or exist in oil of Dippel, or are produced during putrefaction.

Hydropyridines—Piperidines—are compounds produced from the pyridines by the action of nascent hydrogen. **Dihydropyridines** and **tetrahydropyridines** are known, the latter known as **piperideines**, but by far the most important of the group is

Piperidine—Hexahydropyridine— $\text{H}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{NH}$ — which is produced by saponification of **piperine** by heating with alcoholic KOH, and is also formed by reduction of pyridine, or by heating pentamethylene-diamine hydrochloride. It is a colorless liquid; b. p. 106° ; having an odor like that of pepper; readily soluble in water and in alcohol. Oxidizing agents rupture the piperidine ring, with formation of aliphatic compounds. When heated with methyl iodide it is converted into **methylpiperidine hydroiodide**,

$$\text{H}_2\text{C} \begin{smallmatrix} \diagup \text{CH}_2\text{CH}_2 \\ \diagdown \text{CH}_2\text{CH}_2 \end{smallmatrix} \text{N} \begin{smallmatrix} \diagup \text{HI} \\ \diagdown \text{CH}_3 \end{smallmatrix}$$

Piperidine and methyl-piperidine are particularly of interest as being the nuclei of a number of vegetable alkaloids. Thus **coniine** is α propyl-piperidine, and **tropine** and **ecgonine**, the basic nuclei of the atropic and cocaine alkaloids, are derivatives of methyl-piperidine (see pp. 425, 427).

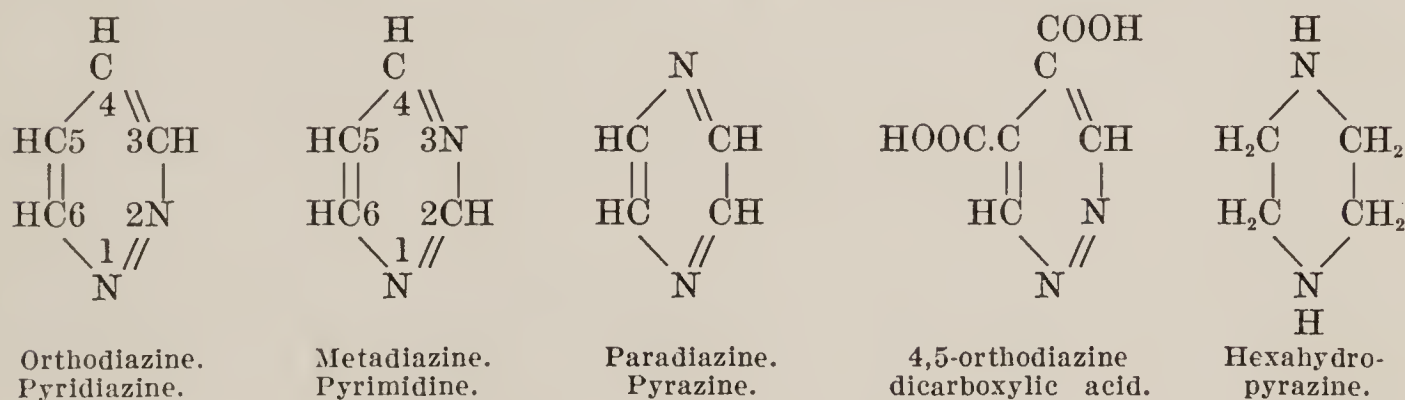
AZINES AND THEIR DERIVATIVES.

The azines are compounds bearing the same relation to pyridine that azoles bear to pyrrole (p. 393), *i.e.*, they are derived from pyridine by substitution of further hetero-atoms in the ring. Oxygen,

sulphur and nitrogen are the only elements known to enter into such ring formation. When but one hetero-atom exists in the ring in addition to the pyridine N, the substance is a derivative of an **oxazine** if it is O, of a **thiazine** if it is S, and of a **diazine** if it is N; and there are three of each class,—ortho, meta and para. Nuclei also exist containing more than two hetero-atoms, O, S, or N, in a six membered ring, and, as these may be like or unlike, such compounds are very numerous and of great variety.

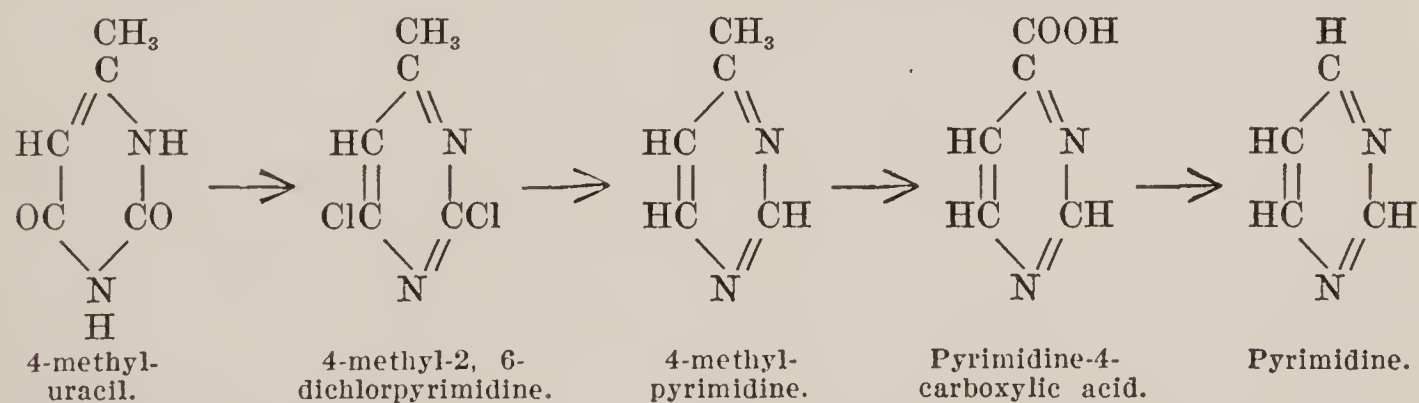
The **oxazines** and **thiazines** are only known in their derivatives.

Diazines.—There exist three isomeric diazines—ortho, meta and para—which are thin, colorless oils, soluble in water, alcohol and ether, insoluble in petroleum ether, neutral in reaction:



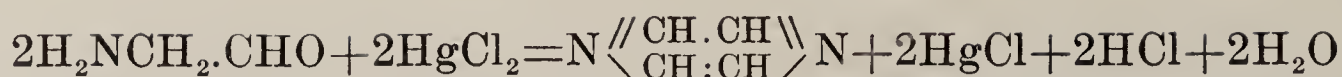
Orthodiazine—Pyridiazine—is obtained by heating the 4, 5-dicarboxylic acid (formulae above): $C_4H_2N_2(COOH)_2 = C_4H_4N_2 + 2CO_2$, which is itself obtained from the tetracarboxylic acid, a product of oxidation of phenazone (below). It has a pyridine-like odor, b. p. 208° . Forms an insoluble, crystalline compound with $AuCl_3$.

Metadiazine—Pyrimidine—is obtained by starting from 4-methyluracil. This is first converted by $POCl_3$ into 4-methyl-2, 6-dichloropyrimidine, which is then reduced by zinc dust to 4-methylpyrimidine, which is then oxidized to the carboxylic acid, and this is decomposed by heat into pyrimidine and carbon dioxide:



The free base is an oil, b. p. 124° , having a penetrating, narcotic odor, which forms a nitrate and a hydrochloride, both of which are completely volatile below 100° . It forms crystalline compounds with $HgCl_2$, $AuCl_3$, and picric acid, but not with $CuSO_4$.

Paradiazine—Pyrazine—is obtained by condensation of amido acetaldehyde by mercuric chloride:



It has a faint heliotrope odor. B. p. 118° . From concentrated aqueous solution it deposits crystals, f. p. 53° , which are extremely volatile. It forms a crystalline compound with CuSO_4 . Pyrazine and its homologues are produced during fermentation, and exist in fusel oils and in commercial amylic alcohol.

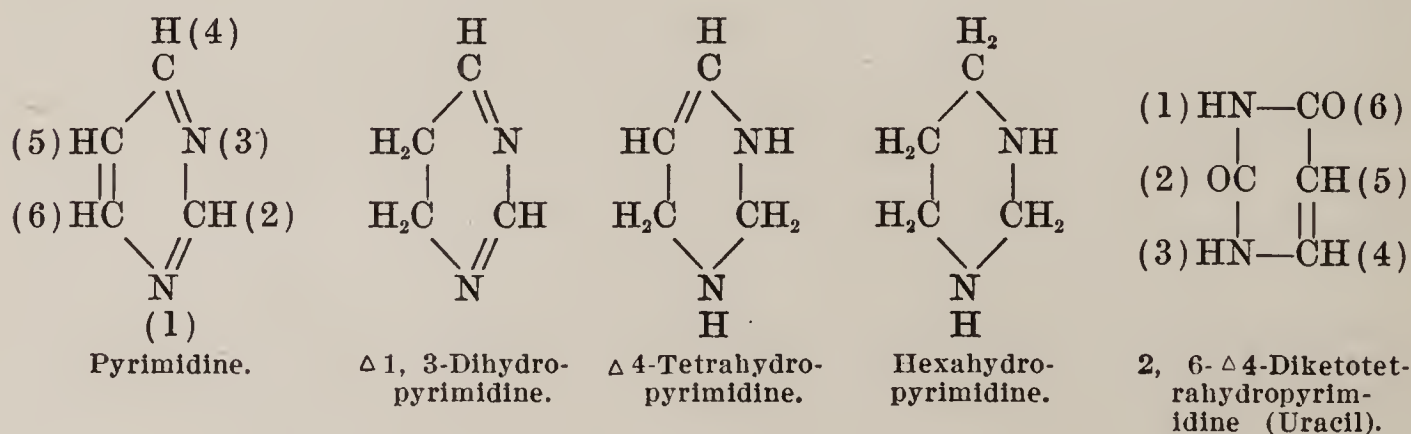
Hexahydro - pyrazine — Piperazine — Diethylene Diamine—
 $\text{HN}\cdot\text{CH}_2\cdot\text{CH}_2$
 $\text{H}_2\text{C}\cdot\text{CH}_2\cdot\text{NH}$ —may be obtained by reduction of para-diazine, but is manufactured from diphenyl-diethylene diamine, $\text{C}_6\text{H}_5\cdot\text{N} \begin{array}{c} \text{<CH}_2\cdot\text{CH}_2\text{>} \\ \text{CH}_2\cdot\text{CH}_2 \end{array}$
 $\text{N}\cdot\text{C}_6\text{H}_5$, which is obtained by the action of ethylene bromide upon aniline. It crystallizes in colorless needles; f. p. 104° ; b. p. 145° ; soluble in water, and deliquescent. It is strongly alkaline and basic, and absorbs carbon dioxide from air. It forms a soluble compound with uric acid and is used medicinally as a solvent for uric acid in lithiasis.

Pyrimidine Derivatives.—The pyrimidine, or myazine compounds which are of medical interest are not referable directly to pyrimidine, or metadiazine itself, but to the hydropyrimidines (formulae below), of which they are ring ketone derivatives, most of which contain the grouping $\text{N}\cdot\text{CO}\cdot\text{N}$, which also exists in urea. They include uric acid and its derivatives, the xanthine bases, and most of the cyclic ureides (p. 316). They are divided into two groups:

I. Compounds containing a single hydropyrimidine ring, more or less modified by substitution. This class includes: (a) **The uracil group**, (b) **The malonylurea group**, (c) **The guanides**.

II. **The purine group.**—Compounds containing a hydropyrimidine nucleus with a glyoxaline ring fused upon it. These compounds would be more properly classified among the condensed heterocyclic compounds (p. 414), but are more conveniently considered here.

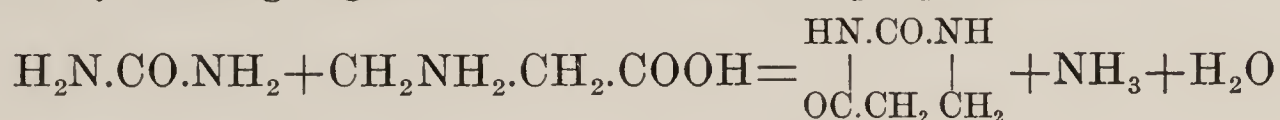
The positions of orientation in the pyrimidine ring have been designated in several different ways, which has led to no little confusion. The notation which will be adopted here is that in which numbers are used, and in which the two nitrogen atoms occupy the 1 and 3 positions, as in the following formulae of pyrimidine and of uracil:



While the above hexagonal expressions are most in conformity with those of other cyclic compounds, and are on that ground preferable to the quadrilateral expression of the formula of uracil, the latter form was adopted for the uracyl, uric acid and xanthine derivatives before their relationship to pyrimidine was recognized, and have since come into such universal use that we feel reluctantly compelled to make use of them for these compounds.

I *a*. **The Uracil Group.**—The physiologically interesting members of this group are 2, 6-diketo derivatives of the unknown tetrahydropyrimidine, sometimes referred to as oxypyrimidine derivatives, a term which more properly applies to compounds containing a phenolic or secondary alcoholic OH as a lateral chain.

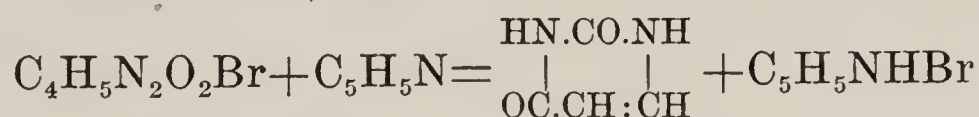
Uracil— $C_4H_4N_2O_2$ —2, 6- Δ 4-diketotetrahydropyrimidine—was first obtained as a product of decomposition of yeast-nucleic acid, and later from other nucleic acids. It is also formed from thymine in autolysis of pancreas, and is probably widely disseminated in animal organisms. It has been obtained synthetically: Hydrouracil, the corresponding hexahydropyrimidine derivative, is first obtained, either by heating together urea and β -amidopropionic acid:



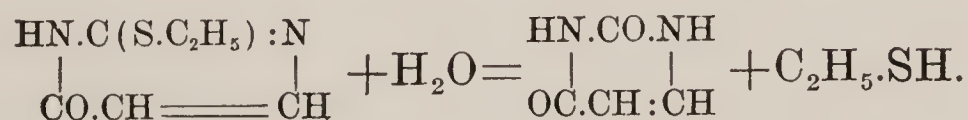
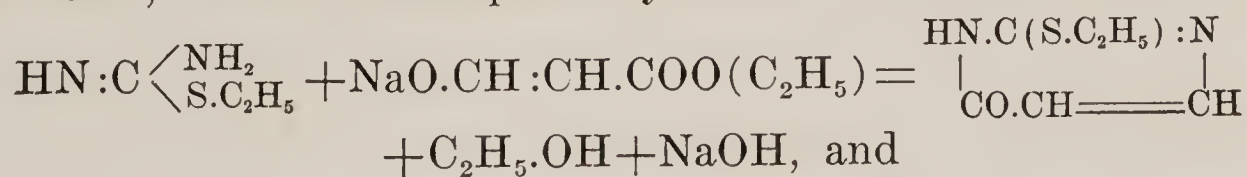
or, more readily, from urea and acrylic acid:



This latter reaction constitutes a general method of synthesis of uracil derivatives, starting from various unsaturated acids, known as Fischer and Roeder's method. The hydrouracil is then converted into a bromine derivative, which is debrominated by pyridine:

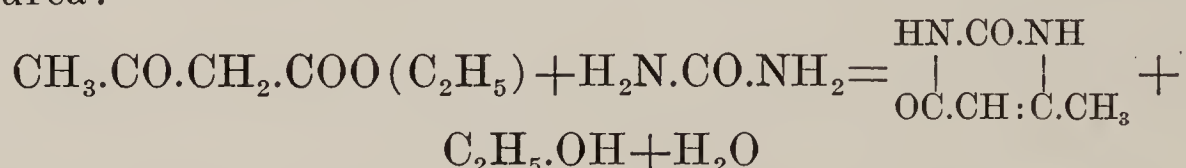


Another general method of synthesis of the uracil compounds is that of Wheeler and Johnson, based upon the fact that alkylpseudothioureas readily condense with ketonic acid esters to form alkylmercaptoketopyrimidines, which are split by boiling with HCl or HBr to ketopyrimidines and mercaptan. Thus ethylpseudothiourea and sodium formylacetic ester condense to 2-ethylmercapto-6-ketopyrimidine, which is decomposed by HBr to uracil and mercaptan:



Uracil crystallizes in rosettes of needles, easily soluble in hot water, difficultly in cold water, almost insoluble in alcohol and ether, easily soluble in ammonia. It does not form compounds with HCl or HNO₃, nor a ppt. with phosphotungstic acid. With AgNO₃ alone it does not ppt., but on addition of NH₄OH a gelatinous ppt. is formed, soluble in excess. It also forms a ppt. with Hg(NO₃)₂. It gives the Weidel reaction, which consists of the production of a red or purple color when chlorine water and a trace of HNO₃ are evaporated with the substance, and the residue is exposed to ammonia. This reaction is characteristic of certain pyrimidine compounds (see Xanthine, p. 410). Two methyluracils are known.

4-Methyluracil—(formula p. 403)—the earliest known of the uracil compounds, is formed by the condensation of acetoacetic ester with urea:

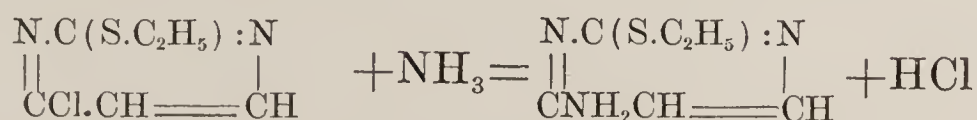


a reaction which constitutes one of the steps in a synthesis of uric acid (p. 406). It is also formed by Fischer and Roeder's method by starting from crotonic acid, CH₃.CH:CH.COOH; and by Wheeler and Johnson's method by starting from methylpseudothiurea and acetoacetic ester. It crystallizes in needles from hot water, and is difficultly soluble in alcohol. It dissolves in NaOH or KOH, forming crystallizable salts. By further methylation it yields dimethyl- and trimethyl-uracil. It also forms chlorine, nitro, amido and phenyl derivatives, and carboxylic acids.

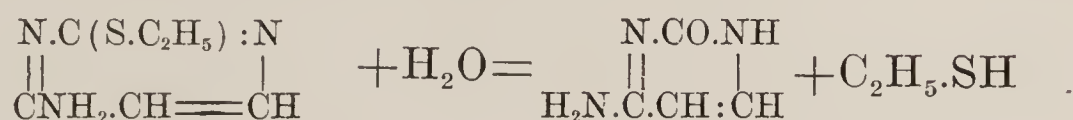
Thymine—5-Methyluracil—(formula p. 403)—is a product of decomposition of thymus-nucleic acid. It is formed synthetically by Fischer and Roeder's method, starting from methacrylic acid, CH₂:C(CH₃).COOH; and by Wheeler and Johnson's method, starting from methylpseudothiurea and sodium formylpropionic ester, NaO.CH \begin{array}{l} \diagup \\ \text{H}_3\text{C} \end{array} \diagdown \text{C.COOH. It crystallizes in quadratic or six-sided prisms; fuses and sublimes at 250°; is difficultly soluble in cold water, easily in hot water, less soluble in alcohol and ether. It is neither distinctly acid nor basic. Its aqueous solution ppts. with Hg(NO₃)₂; with HgCl₂ only after addition of NaOH to slight alkalinity, and with AgNO₃ only after addition of NH₄OH. It decolorizes bromine water. On nitration and subsequent reduction it yields a compound which gives the Weidel reaction. It is pptd. by phosphotungstic acid.

4-Phenyluracil—C₄H₃N₂O₂.C₆H₅—is formed by condensation of urea and benzoylacetic ester, CH₂(CO.C₆H₅).COO(C₂H₅); by Fischer and Roeder's method, starting from cinnamic, or β-phenylacrylic acid, CH(C₆H₅):CH.COOH; and by Wheeler and Johnson's method, starting from methylpseudothiurea and sodium benzoylacetate. 5-Phenyluracil is also known.

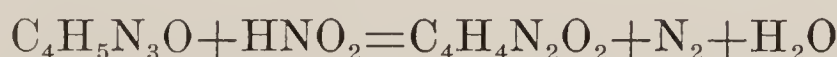
Cytosine—6-amido- 2 keto - Δ 4, 6-dihydropyrimidine—(formula below)—obtained from thymus-nucleic acids, herring and sturgeon melt, pancreas, yeast and wheat, is not properly a uracil derivative, as it does not contain two CO groups, and it is a dihydro pyrimidine, not a tetrahydropyrimidine, derivative. It is obtained synthetically by Wheeler and Johnson's method: 2-ethylmercapto-6-ketopyrimidine is obtained as described above (uracil). This is then converted by PCl_5 into 2-ethylmercapto-6-chloropyrimidine, which with alcoholic ammonia produces 2-ethylmercapto-6-amidopyrimidine:



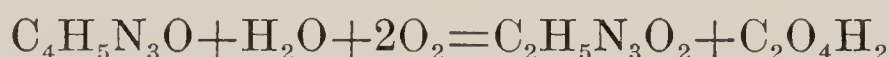
and this is split by HBr into cytosine and mercaptan:



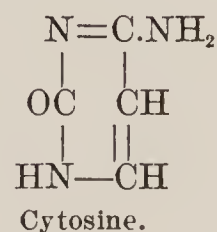
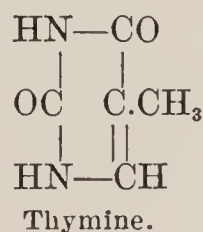
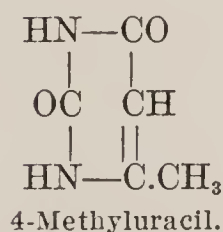
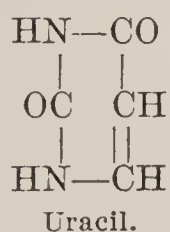
Cytosine crystallizes in pearly plates, difficultly soluble in water. It forms a hydrobromide, chloroplatinate, picrate, nitrate and two sulphates, which are all crystalline. It is pptd. by phosphotungstic acid, by AgNO_3 , and by Ba(OH)_2 in excess. It gives the Weidel reaction, although it contains but one CO. Nitrous acid converts it into uracil:



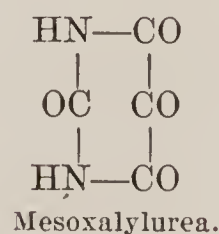
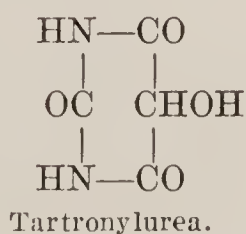
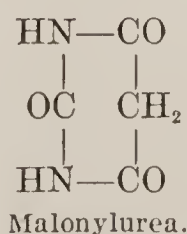
as guanine is converted into xanthine, and adenine into hypoxanthine (p. 411). When oxidized by BaMn_2O_8 it yields biuret and oxalic acid:



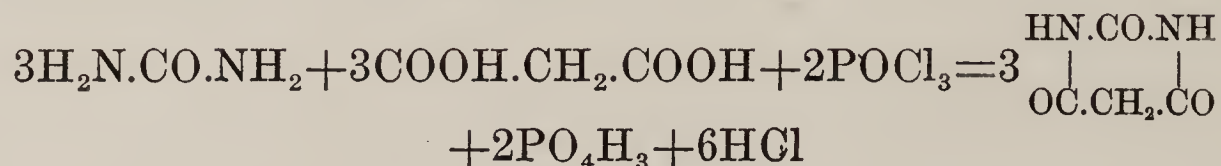
The relations of the uracils and cytosine are shown in the following formulæ:



Ib. The Malonylurea Group.—The members of this group are tri- or tetraketo-hexahydropyrimidine compounds, all of which are derivable from malonylurea by substitution in the CH_2 group of malonic acid. The three principal members of the group are:



Malonylurea—Barbituric Acid—2, 4, 6-Triketohexahydropyrimidine— $C_4H_4N_2O_3$ —is produced by the action of $POCl_3$ upon a mixture of urea and malonic acid:



It is also formed by the action of concentrated H_2SO_4 on alloxantin (below). It crystallizes with 4 Aq., is efflorescent, sparingly soluble in cold water, readily soluble in hot water. It behaves as a dibasic acid. It is decomposed by boiling alkalies:

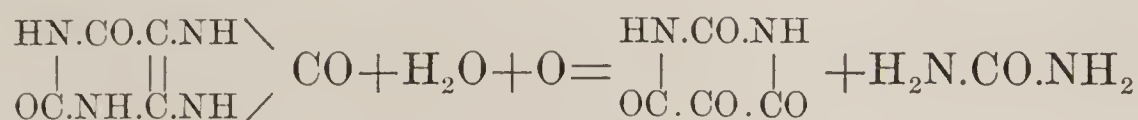


In malonylurea the hydrogen atoms of the CH_2 group exhibit the same mobility that they do in malonic ester, and are replaceable by sodium, which is in turn replaceable by alkyls. Thus **dimethylmalonylurea**, $OC \begin{array}{c} \text{NH.CO} \\ \diagup \quad \diagdown \\ \text{NH.CO} \end{array} C(CH_3)_2$, may be produced either by the successive action of Na and CH_3I upon malonylurea, or by the action of $POCl_3$ upon urea and dimethylmalonic acid. The last named acid is produced when dimethylmalonylurea is hydrolyzed by KOH. Dimethylmalonylurea is isomeric with **malonyldimethylurea**, $OC \begin{array}{c} N(CH_3).CO \\ \diagup \quad \diagdown \\ N(CH_3).CO \end{array} CH_2$, obtained by the action of $POCl_3$ upon malonic acid and dimethylurea. **Diethylmalonylurea**, $OC \begin{array}{c} \text{NH.CO} \\ \diagup \quad \diagdown \\ \text{NH.CO} \end{array} C(C_2H_5)_2$, is similarly obtained, and has been used as a hypnotic under the name *veronal*.

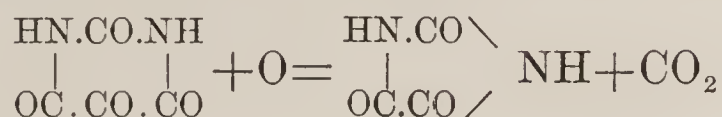
Tartronylurea—Dialuric Acid—2, 4, 6-triketo-5-oxyhexahydropyrimidine— $C_4H_4N_2O_4$ —is produced, along with oxaluric acid by reduction of alloxan, it containing a secondary alcoholic group in the 5 position, where alloxan contains a ketone group (formulæ p. 403). It is converted by nitrous acid into allantoin. By exposure to air and moisture tartronylurea forms **alloxantin**, $C_8H_4N_4O_7$, in which reaction probably one molecule of tartronylurea is oxidized to alloxan, which condenses with a second molecule of tartronylurea. Alloxantin is also formed by reduction of alloxan, and by oxidation of uric acid. It forms sparingly soluble crystals, which turn red on exposure to air. **Murexide** is the ammonium salt of the unknown **purpuric acid**, $C_8H_5N_5O_6$, derived from alloxantin by substitution of NH for O, and, like that substance, containing two hydropyrimidine nuclei. It is produced by heating alloxantin with NH_3 , or by evaporating nitric acid on uric acid, and adding ammonia to the residue (murexide test, p. 408). The product of the Weidel reaction, in which chlorine water with a trace of HNO_3 is used as an oxidant (p. 402), is also probably murexide. Murexide crystallizes in short, red prisms, having a greenish reflection, and forming a red

powder when ground. It is difficultly soluble in cold water, insoluble in alcohol and ether.

Alloxan—Mesoxalylurea—2, 4, 5, 6-Tetraketohexahydropyrimidine— $C_4H_2N_2O_4$ —is a product of the limited oxidation of uric acid, alloxantin, or murexide. Uric acid oxidized by dilute HNO_3 at 60° to 70° yields alloxan and urea:



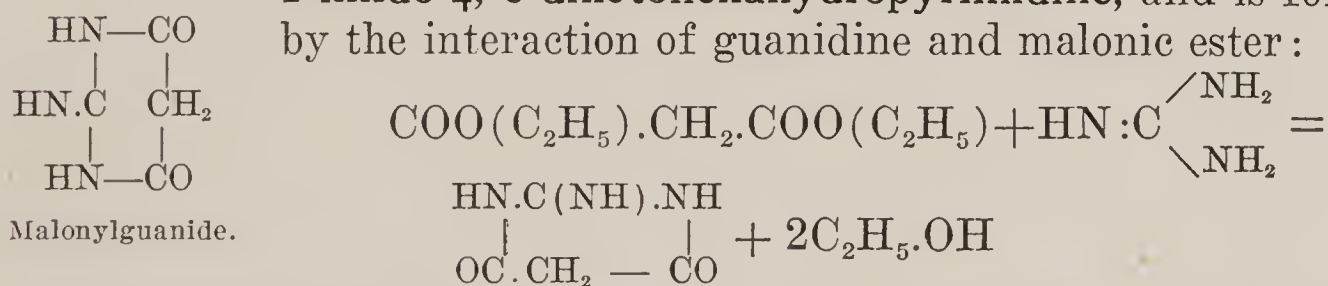
It has been found in the intestinal mucus in diarrhea. It forms prismatic crystals, readily soluble in water, which turn red in air, are acid in reaction, and stain the skin red. Reducing agents convert it into alloxantin; and by oxidation it yields oxalylurea:



When heated with $Ba(OH)_2$ the cyclic nucleus is broken, and alloxanic acid is formed:

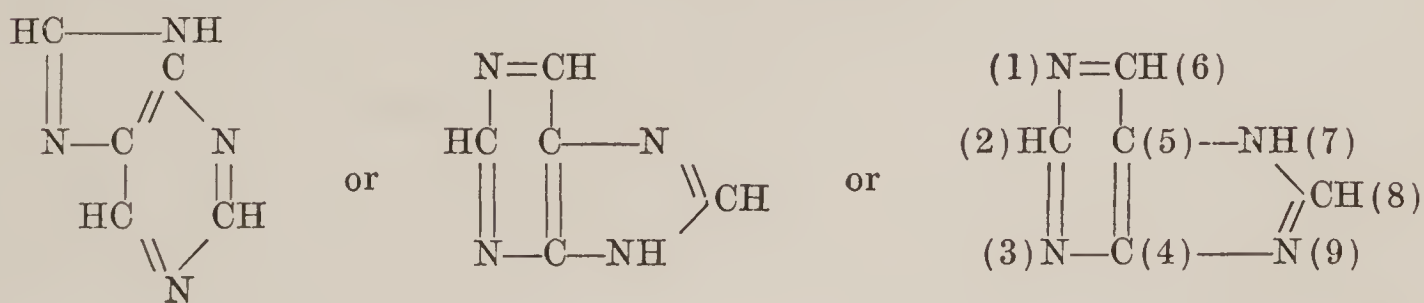


Ic. The guanides are derivatives of malonylguanide, which is 2-imido-4, 6-diketohexahydropyrimidine, and is formed by the interaction of guanidine and malonic ester:



The derivatives are formed, as are those of malonic ester, and of malonylurea, by substitution in the CH_2 group.

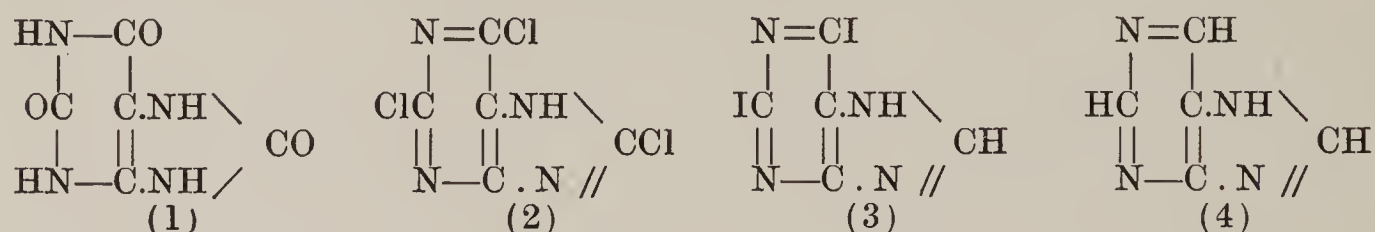
II. The purine group.—The compounds of this group, which includes uric acid, the xanthine bases, caffeine, etc., are derivatives of purine, whose molecule consists of a pyrimidine ring, with a glyoxalin ring fused upon it at the 4 and 5 positions:



the last of which is the formula now generally adopted.

Some of the derivatives are referable to purine itself, others to the methylpurines, in which CH_3 is substituted for H in one or more of the positions, 2, 6, 8, and 7 or 9.

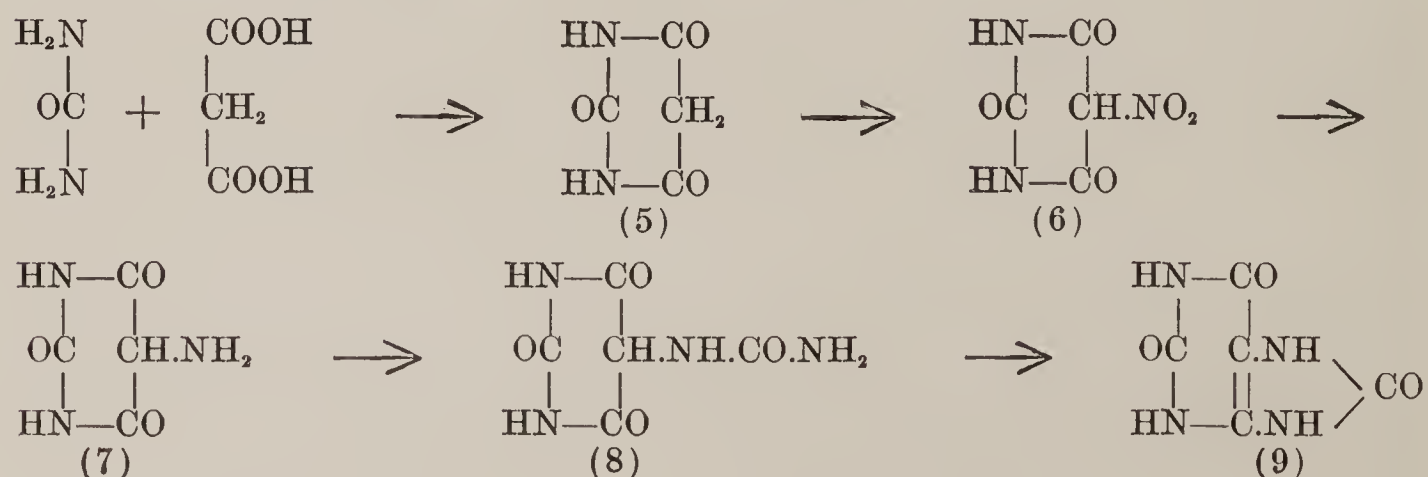
Purine— $C_5H_4N_4$ —is obtained by starting from uric acid (1). This is converted by $POCl_3$, first into 8-keto-2, 6-dichlorpurine and then into 2, 6, 8-trichlorpurine (2). By the action of HI and PH_4I this is converted into 2, 6-diiodopurine (3), which by boiling with zinc in an atmosphere of CO_2 yields purine (4) :



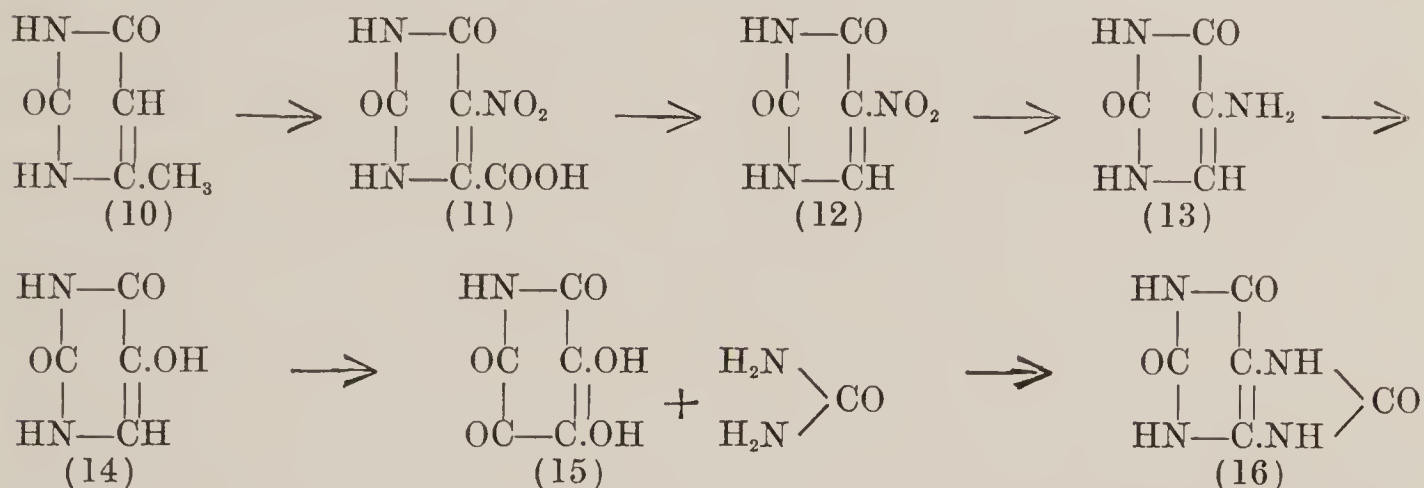
Purine crystallizes in small needles, f. p. 212° , very soluble in cold water and in warm alcohol. It is neutral in reaction, but forms salts with both acids and bases. Its solutions ppt. with $AgNO_3$, phosphotungstic acid and tannin; not with KI , Nessler's reagent or $K_4Fe(CN)_6$. It withstands oxidizing agents. Its reaction with Br is characteristic; in its solution in concentrated HCl , Br forms a fine reddish yellow, crystalline mass, soluble on warming, and crystallizing again on cooling.

Uric Acid—Lithic Acid—2, 6, 8-Triketopurine—(formula 1, above), $C_5H_4N_4O_3$ —occurs in the urine of man and of the carnivora, in combination, chiefly as its disodic salt; in the urine of the herbivora, in which ordinarily it is replaced by hippuric acid, when, in early life and during starvation, they are, for the time being, practically carnivora; in some urinary calculi, in the so-called "chalky deposits," or "tophi," in the joints of the gouty; very abundantly in the excretions of serpents, tortoises, birds, molluscs and insects, and in guano; in smaller amount in the blood and tissues. It is best obtained from guano or from the solid urine of serpents, which consists almost entirely of ammonium urate.

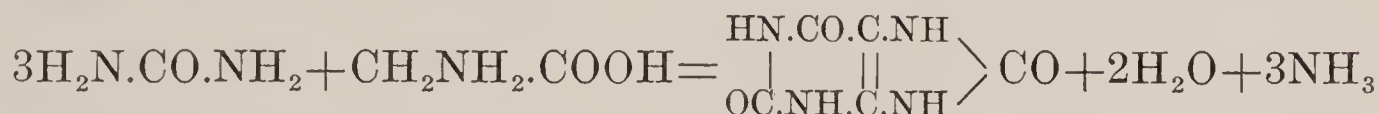
Uric acid is obtained synthetically: (1) From monochloracetic acid and urea. Monochloracetic acid is converted into malonic acid; this is then condensed with urea to malonylurea (5 below); this by HNO_3 to nitromalonylurea (6); this by reduction to amidomalonylurea (7); this by condensation with urea to pseudouric acid (8); and this by dehydration to uric acid (9) :



(2) From acetoacetic ester and urea: 4-Methyluracil is first obtained from acetoacetic ester and urea (10 below). By the action of fuming HNO_3 and H_2SO_4 this is converted into the 5-nitro-4-carboxylic acid (11); this by heat to 5-nitrouracil (12); this by reduction to a mixture of 5-amidouracil (13), and 5-oxyuracil, or **isobarbituric acid** (14); the former of which is converted into the latter by dilute acids. By oxidation with bromine water 5-oxyuracil yields 4, 5-dioxyuracil, or **isodialuric acid** (15), which in presence of concentrated H_2SO_4 condenses with urea to uric acid (16):



(3) From amidoacetic acid and urea, by heating glycocoll with excess of urea to $200^\circ\text{--}230^\circ$:



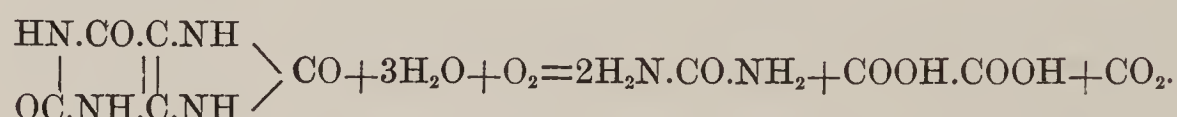
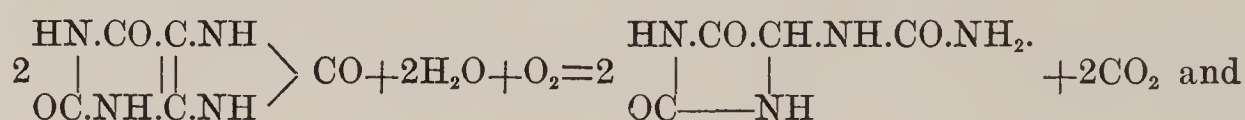
When pure, uric acid crystallizes in small, colorless, rhombic, rectangular or hexagonal plates, or in rectangular prisms. As crystallized from the urine, it is more or less colored by the urinary pigments, and the angles of the crystals are rounded to produce lozenge shapes, which are arranged in bundles, crosses or daggers. It is very sparingly soluble in water, requiring 36,480 parts of pure water for its solution at 18° . In ordinary distilled water it is more soluble, 1:15,000 cold, and 1:1,900 boiling. It is soluble in 1,900 parts of a 2 per cent. solution of urea, insoluble in alcohol and ether. Cold HCl dissolves it more readily than water, and on standing deposits it in colorless rectangular plates. Its aqueous solution is acid to litmus, but tasteless and odorless. It also dissolves unchanged in concentrated H_2SO_4 , and is deposited from the solution on dilution with water. It dissolves in KOH and NaOH solutions with formation of urates.

Uric acid is decomposed by heat, yielding as final products ammonia, carbon dioxide, urea and hydrocyanic and cyanuric acids. Nascent hydrogen reduces it to xanthine (p. 410). With Cl , Br , or I at ordinary temperatures it forms oxalic and parabanic acids, alloxan and ammonium cyanate. Heated with Cl it yields cyanuric acid and HCl . It dissolves in cold HNO_3 , with effervescence and formation of

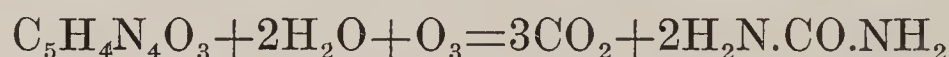
alloxan, alloxantin and urea; with hot HNO_3 parabanic acid is produced. A yellow or red residue remains when HNO_3 is evaporated on uric acid, and this assumes a fine red-violet or purple color when moistened, in the cold, with NH_4OH , NaOH or KOH (murexide reaction). On heating with concentrated HCl to 170° uric acid is decomposed to glycocoll, ammonia and carbon dioxide:



and, as ammonia and carbon dioxide are the products of hydrolysis of urea, this decomposition is the reverse of the synthesis described above (p. 406). When oxidized by lead peroxide uric acid yields allantoin, carbon dioxide, urea and oxalic acid, two distinct reactions occurring at the same time:



Certain bacteria decompose uric acid according to the equation:



Uric acid is decomposed by sodium hypobromite, giving off 47 per cent. of its nitrogen in the cold, or the whole when heated. It reduces the salts of copper on prolonged boiling in alkaline solution. The xanthine bases (p. 409) and uric acid are pptd. by a mixture of equal volumes of a 13 per cent. solution of CuSO and a 50:100 solution of NaHSO_3 (Krüger-Wolff reagent), which does not ppt. urea. Uric acid is pptd. from solutions containing magnesia mixture, by ammoniacal AgNO_3 , as silver-magnesium urate. It is pptd., as ammonium urate, by complete saturation of its solutions with NH_4Cl .

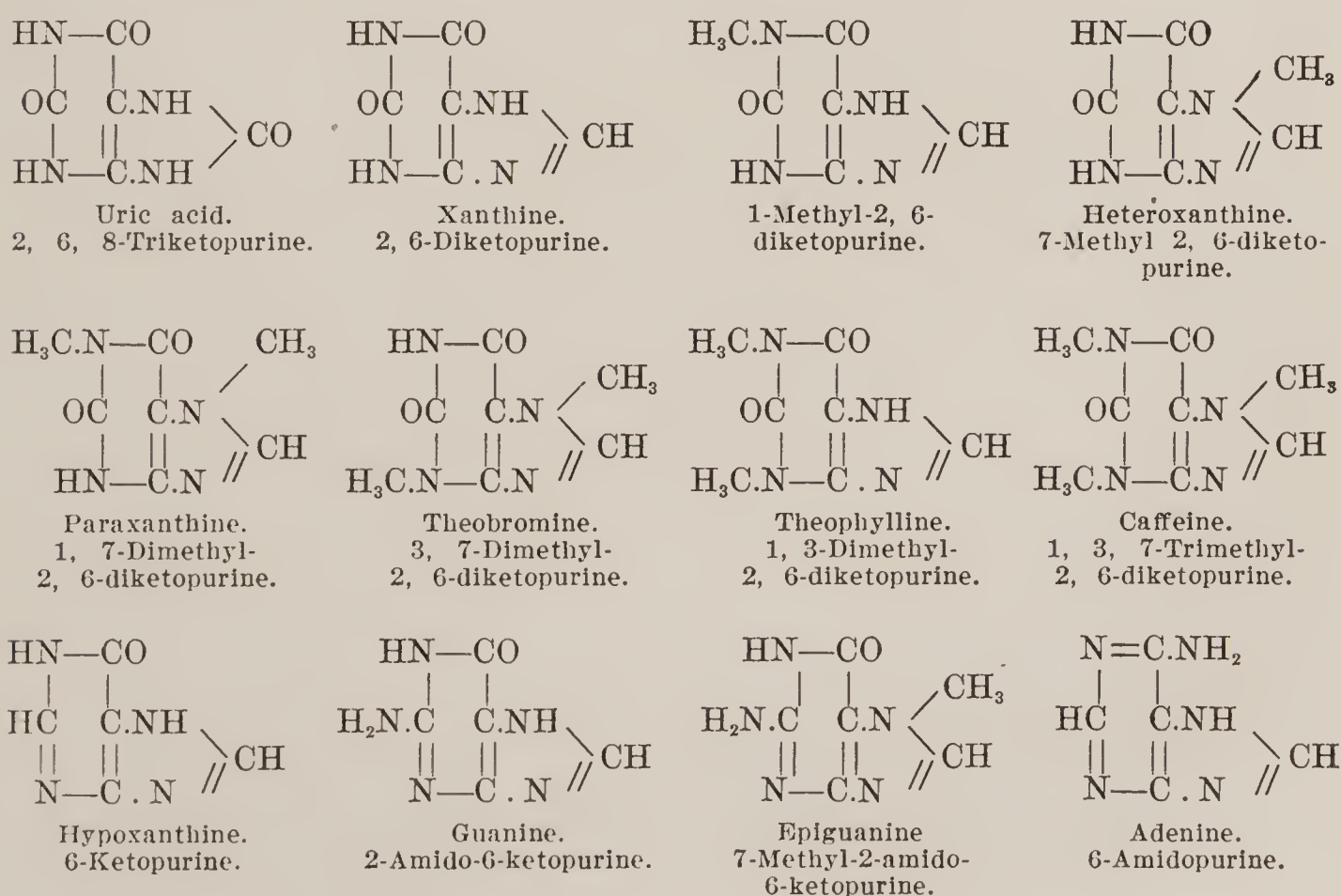
Uric acid behaves as a dibasic acid. The monometallic salts are formed by dissolving the acid in solutions of the metallic carbonates, or by treating solutions of the dimetallic salts with carbon dioxide. The dimetallic salts are formed by dissolving the acid in solutions of the metallic hydroxides, free from carbonate. **Mono-ammonium urate**, $\text{C}_5\text{H}_3\text{N}_4\text{O}_3(\text{NH}_4)$, exists in the solid urines of the lower animals, and in urinary sediments and calculi. It is very sparingly soluble in water. **Dipotassic urate** is alkaline in taste, absorbs CO_2 from the air, and is soluble in 44 parts of cold H_2O . **Disodic urate** forms nodular masses, soluble in 77 parts of cold water, and absorbs CO_2 from the air. It is probably in this form of combination that uric acid exists normally in the urine. **Monosodic urate** is much less soluble, requiring 1,200 parts of water for its solution. It exists, generally amorphous, in urinary sediments (amorphous urates) and calculi, and in the arthritic deposits of the gouty, sometimes beautifully crystalline. **Monocalcic urate**, soluble in 603 parts of cold water, also occurs occasionally in urinary sediments and calculi, and in "chalk stones." **Monolithic urate**, $\text{C}_5\text{H}_3\text{N}_4\text{O}_3\text{Li}$, crystallizes in needles, soluble in 60 parts of water at 50° , or in 368 parts at 19° . It is chiefly with a view to the formation of this, the most soluble of the monometallic urates, that the salts of lithium

are given to patients suffering from the uric acid diathesis. Two salts of uric acid with organic bases are still more soluble. **Piperazine urate** dissolves in 50 parts of water at 17° and **lysidine urate** in 6 parts of water.

The **Xanthine, Alloxuric, Purine, or Nuclein Bases**—form a series of which uric acid is the most highly oxidized member, and which, like uric acid, are purine derivatives:

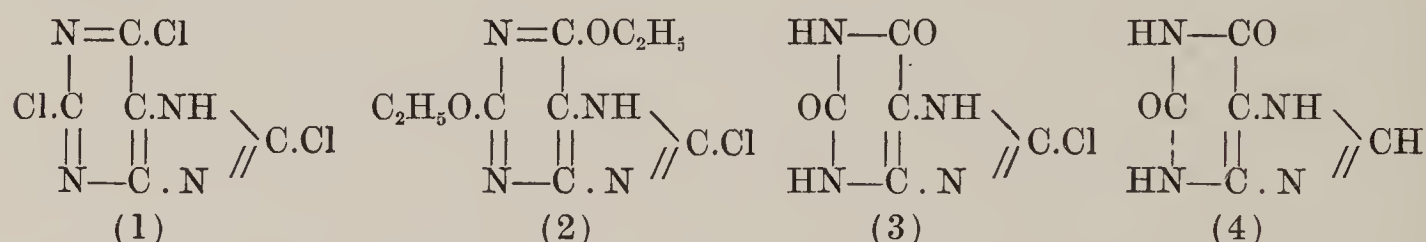
Uric acid,	$C_5H_4N_4O_3$	Heteroxanthine,	$C_5H_3(CH_3)N_4O_2$
Xanthine,	$C_5H_4N_4O_2$	Paraxanthine,	$C_5H_2(CH_3)_2N_4O_2$
Hypoxanthine,	$C_5H_4N_4O$	Theobromine,	$C_5H_2(CH_3)_2N_4O_2$
Guanine,	$C_5H_5N_5O$	Theophylline,	$C_5H_2(CH_3)_2N_4O_2$
		Caffeine,	$C_5H(CH_3)_3N_4O_2$
Adenine,	$C_5H_5N_5$	Epiguanine,	$C_5H_4(CH_3)N_5O$

Of the substances named in the first column, xanthine, hypoxanthine and guanine are, like uric acid, ketopurines, also called oxypurines, while adenine contains no oxygen; and guanine and adenine further differ from xanthine and hypoxanthine, in that they contain an amido group. Those in the second column are methyl derivatives of xanthine or of guanine, to which they bear the same relation that the methyluric acids do to uric acid. Besides the substances above enumerated, **carnine**, $C_7H_8N_4O_3$ and **episarkine**, $C_4H_6O_3$ (?) probably belong in this class. Adenine, guanine, hypoxanthine and xanthine are products of decomposition of nucleic acids, which are themselves products of decomposition of nucleoproteids. The relations of the xanthine bases to each other and to uric acid are shown in the following formulæ:



Xanthine—*Xanthic Acid*—*Urous Acid*—**2, 6-Diketopurine**—**2, 6-Dioxypurine**— $C_5H_4N_4O_2$ —occurs in a rare form of vesical calculus, in the pancreas, spleen, liver, thymus, kidneys, brain, and in the melt of fishes. It is a normal constituent of the urine in small amount. Xanthine, hypoxanthine, guanine, and adenine are products of decomposition of the nucleins.

Xanthine is obtained synthetically, either by the deamidation of guanine by nitrous acid (p. 412); or by Fischer's method, which, in its variations, permits of the formation of the several xanthine bases from uric acid through the chloropurines. In the formation of xanthine, uric acid is converted into 2, 6, 8-trichloropurine (1) by $POCl_3$. By heating with excess of sodium ethylate this is converted into 2, 6-diethoxy-8-chloropurine (2). This is saponified by HCl to 2, 6-diketo-8-chloropurine (3), which is then reduced by HI to xanthine (4)



Xanthine and hypoxanthine are also formed in small amount by the direct reduction of uric acid by nascent formic acid. By methylation xanthine yields theobromine and caffeine.

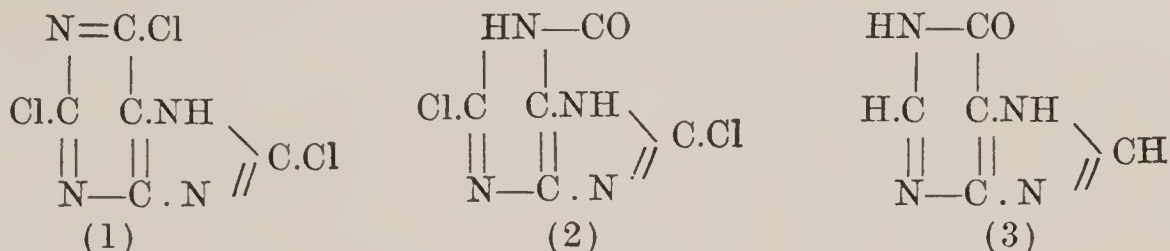
It is usually amorphous, but may form crystalline plates. It is very sparingly soluble in water, 1:14,500 at 16 degrees, 1:1,400 at 100 degrees; insoluble in alcohol or ether; readily soluble in alkalis. Its ammoniacal solution gives a gelatinous ppt. with $AgNO_3$. If dissolved in HNO_3 , and the solution evaporated, it leaves a yellow residue which, with $NaOH$, turns reddish-yellow, then purple-red (xanthine reaction). It gives the Weidel reaction (p. 402). As this reaction is given with uracil, cytosine, uric acid, xanthine, all the methylxanthines, and alloxan, but not by hypoxanthine, guanine, or adenine, it would seem to be characteristic of those pyrimidine compounds which contain the group $N.CO.N$, and notably of those containing two ketone groups, although cytosine contains but one such group.

Methylxanthines.—1-Methylxanthine, 7-methylxanthine, or **heteroxanthine**, and 1, 7-dimethylxanthine, or **paraxanthine** occur in small quantities in the urine. With the xanthine reaction 1-methylxanthine gives an orange color; the others are negative. **Theobromine**, or 3, 7-dimethylxanthine, occurs in the seeds of *Theobroma cacao* in the proportion of about 2 per cent. It is a crystalline powder, bitter in taste; difficultly soluble in water, alcohol, ether and chloroform; soluble in acids, with which it forms salts; soluble in NH_4OH . By partial demethylation it yields heteroxanthine. With $AgNO_3$ it forms a crystalline ppt., which, heated with methyl iodide, yields caffeine. Theobromine and caffeine have both been obtained synthetically by methylation of xanthine, formed by oxidation of guanine (p. 411). **Theophylline**, or 1, 3-dimethylxanthine, occurs in

tea extract. It is formed from 1, 3-dimethyluric acid, and is manufactured for use as a diuretic, from uric acid. **Caffeine**, or *theine*, or *guaranine*, or 1, 3, 7-trimethylxanthine, exists in coffee, tea, Paraguay tea, guarana and other plants, and may be produced from 1, 3, 7-trimethyluric acid. It crystallizes in long, silky needles; faintly bitter; soluble in 75 parts of water at 15 degrees; less soluble in alcohol and ether. With HNO_3 , evaporation, and addition of NH_4OH it gives a purple color.

Hypoxanthine—Sarkine—6-Ketopurine—6-Oxypurine— $\text{C}_5\text{H}_4\text{N}_4\text{O}$ occurs as a constituent of the nucleins in the same situations as xanthine; also in notable amount in the blood of leukemia, and in the melt of salmon and carp; also in numerous seeds and pollen of plants. It is a product of the decomposition of nucleins by acids, by peptic and tryptic digestion, and by putrefaction.

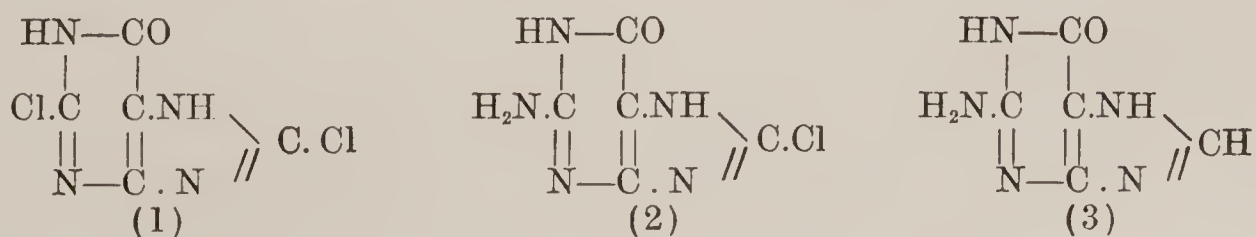
Hypoxanthine is obtained synthetically, either by deamidation of adenine by nitrous acid (adenine, p. 412); or by Fischer's method from uric acid through 2, 6, 8-trichloropurine (xanthine, p. 410), (1). This is converted into 2, 8-dichloro-6-ketopurine (2) by KOH ; and this is reduced by HI and PH_4I to hypoxanthine (3):



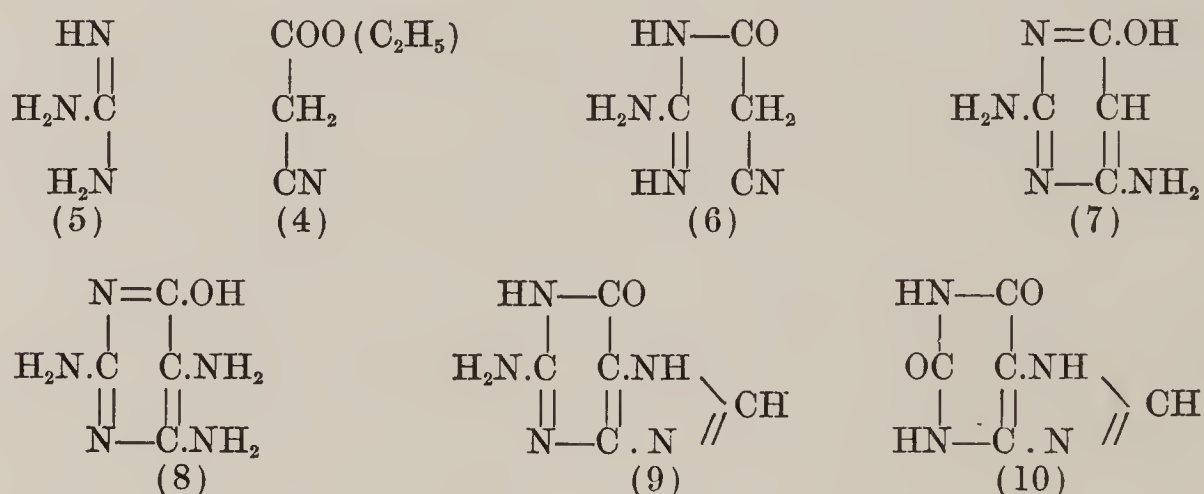
It crystallizes in small, colorless needles; soluble in 300 parts of cold water, or in 75 parts of boiling water; soluble in acids and in alkalis. Its ammoniacal solution forms a ppt. with AgNO_3 . Fuming HNO_3 oxidizes it to nitroxanthine. It does not give the Weidel reaction. When acted upon by zinc and HCl , and then treated with excess of alkali, it forms a ruby-red solution, which turns brown-red (Kossel's reaction).

Guanine—2-Amido-6-ketopurine—occurs abundantly in guano, and as the principal constituent of the excrement of spiders; in less amount, as a constituent of guanylnucleic acid, in the spleen, liver, pancreas, in the melt of the salmon, in the scales and swimming bladders of certain fishes, in normal urine in traces, in the blood in leukemia; and in the young leaves and pollen of certain plants.

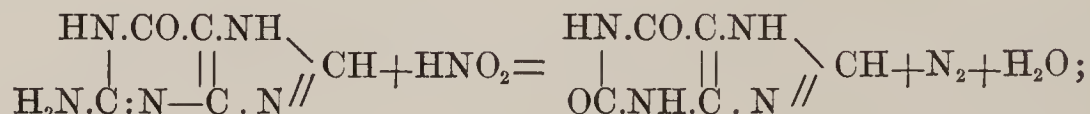
Guanine is produced synthetically in two ways: By Fischer's method, proceeding as in the synthesis of hypoxanthine (above) to the formation of 2, 8-dichloro-6-ketopurine (1). This is converted by heating with alcoholic ammonia at 150° into 2-amido-8-chloro-6-ketopurine (2); which is reduced by HI to guanine:



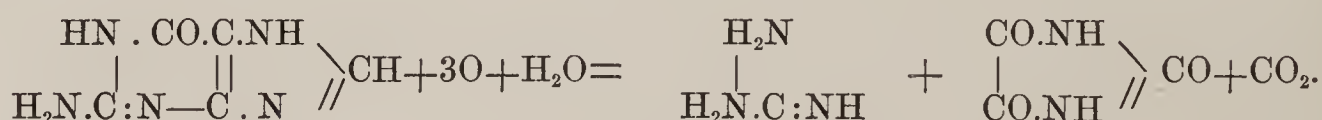
By Traube's synthesis, starting from cyanoacetic ester (4) and guanidine (5), which condense to cyanoacetic guanide (6). This, by union of the amide and cyanogen groups, forms an amidine, and the six-membered ring closes to 2, 4-diamido-6-oxypyrimidine (7). This, by addition of NaNO_2 to solution of the base, forms a rose-colored isonitroso compound, neither basic nor acid, which on reduction by H_2S forms 2, 4, 5-triamido-6-oxypyrimidine (8), which is a strong diacid base, and which, on boiling with strong formic acid, forms guanine (9):



Guanine is deamidated by nitrous acid with formation of xanthine (10):



and xanthine, in turn, may be methylated to theobromine and caffeine. Guanine is oxidized by $\text{KMnO}_4 + \text{HCl}$, with formation of guanidine and oxalylurea:

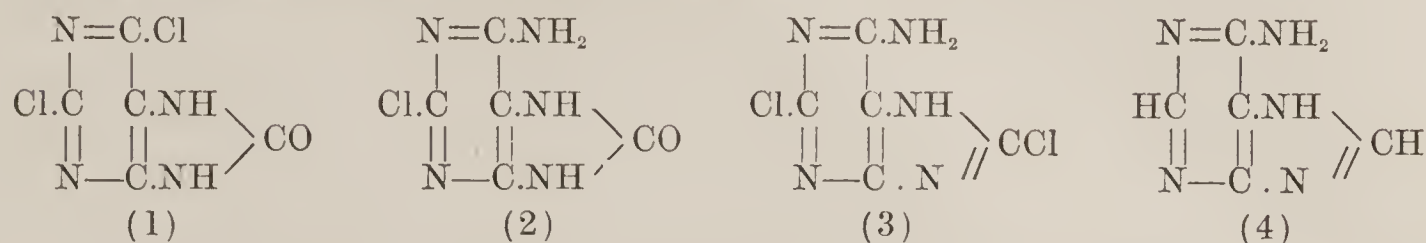


Guanine is a white or yellowish, amorphous and odorless powder: almost insoluble in water, alcohol and ether; readily soluble in acids and alkalis. It forms crystalline ppts. with silver nitrate and with picric acid. It gives the xanthine reaction with HNO_3 and NaOH ; but it does not respond to the Weidel reaction.

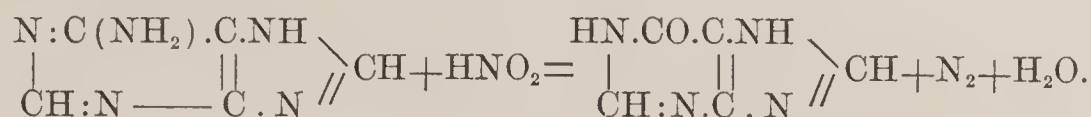
Adenine—6-Amidopurine— $\text{C}_5\text{H}_5\text{N}_5$ —exists, in nucleic acids, widely disseminated in nucleated cells, most abundantly in carp-melt and in the thymus gland. It occurs in the blood and urine in leukemia, and also exists in yeast and abundantly in tea leaves.

It is formed synthetically by Fischer's method: By the action of POCl_3 upon potassium urate 2, 6-dichloro-8-ketopurine (1) is produced. This is converted into 2-chloro-6-amido-8-ketopurine (2) by

NH_3 . This is converted by POCl_3 into 2, 8-dichloro-6-amidopurine (3); which is reduced by HI to adenine (4):



As guanine is deamidated to xanthine, so adenine, on deamidation, yields hypoxanthine:

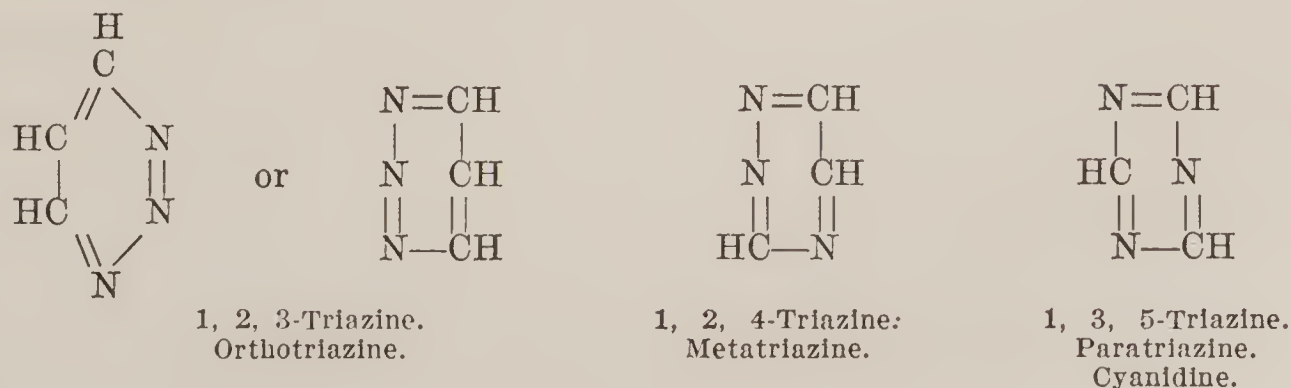


Adenine crystallizes in nacreous plates, or in long needles, with 3 Aq, which they lose at 100° , although they suddenly become opaque at 53° , a property characteristic of adenine. Very soluble in hot water, it requires 1,086 parts of cold water for its solution; insoluble in cold alcohol, ether and chloroform; readily soluble in acids and alkalies, with which it forms compounds. Its solubility in ammonia is less than that of hypoxanthine, but greater than that of guanine. It forms crystalline, difficultly soluble compounds with silver nitrate and with picric acid. It is not reddened by warming with HNO_3 , and moistening the residue with alkali; does not respond to the Weidel reaction, but behaves like hypoxanthine towards Kossel's reaction.

Carnine— $\text{C}_7\text{H}_8\text{N}_4\text{O}_3$ —is obtained from Liebig's meat extract, and has also been found in the muscular tissues of fishes and frogs, and in the urine. It is isomeric with the dimethyluric acids. It forms chalky, microscopic crystals, readily soluble in hot water, sparingly soluble in cold water, insoluble in alcohol and ether. It forms compounds with acids and with alkalies, similar to those of hypoxanthine. Chlorine, bromine and nitrous acid convert it into hypoxanthine, with elimination of the elements of acetic acid. It does not respond to the Weidel reaction.

Epiguanine— $\text{C}_6\text{H}_7\text{N}_5\text{O}_3$.—Besides 7-methylxanthine, which is heteroxanthine, and 7-methyluric acid, similar derivatives of hypoxanthine, guanine and adenine have also been obtained synthetically. 7-Methyl-guanine is epiguanine, which occurs in minute quantity in the urine. **Episarkine** is possibly identical with epiguanine.

Triazines—are compounds containing three nitrogen atoms in a six-membered ring:

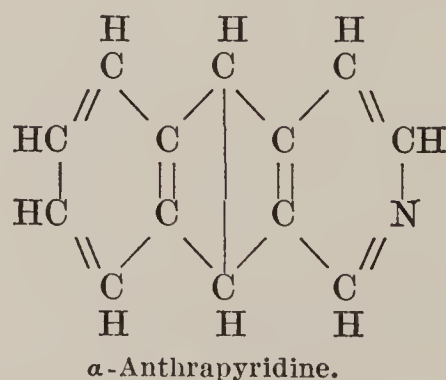
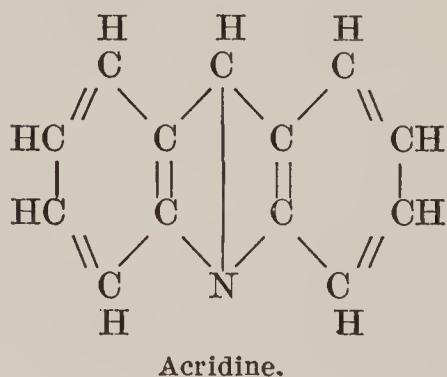
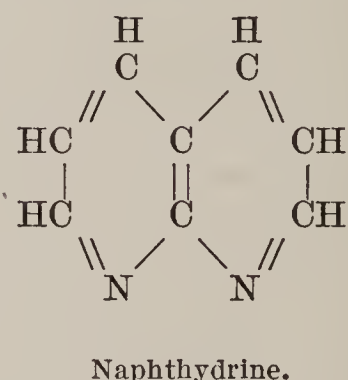
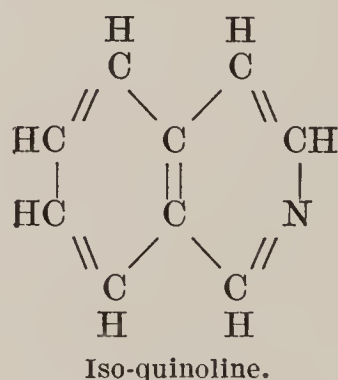
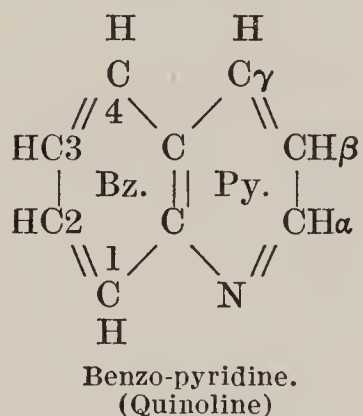
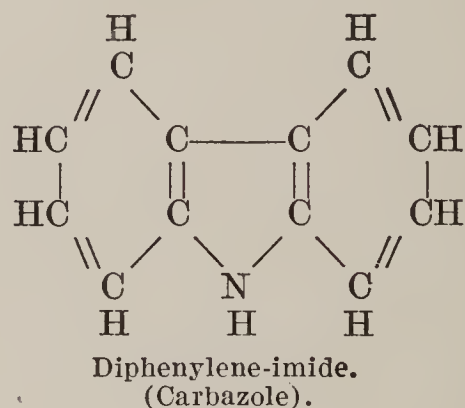
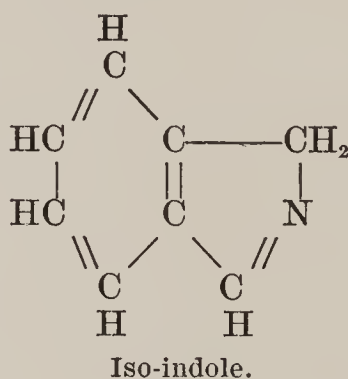
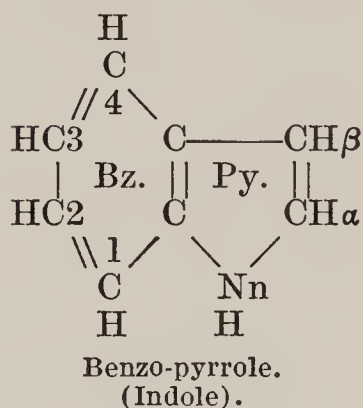


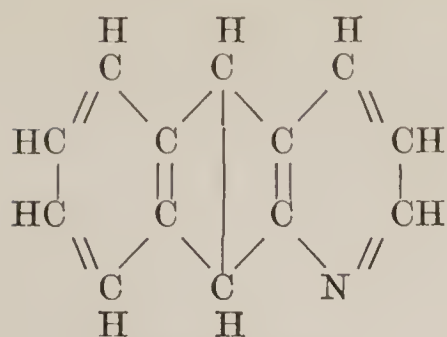
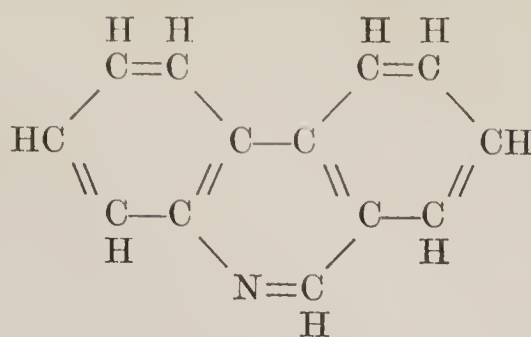
The parent ortho- and meta-compounds are not known, but many of their derivatives have been obtained, none of which is, however, of medical interest.

Para-, or γ -triazine, also called **cyanidine**, is the still unidentified trihydrocyanic acid, which is the parent substance of certain metallocyanides, and of the cyanuric compounds (p. 307).

B. CONDENSED HETEROCYCLIC COMPOUNDS.

These compounds, which are more numerous than the corresponding carbocyclic compounds, may be considered as being derived from the latter by substitution of N for methine, $=CH-$, or of O, S, or NH in a bivalent position, or, as in the case of iso-indole (below), by substitution and modification of internal linkage. The number of these substances is still further increased by the existence of four ringed-compounds, such as the anthraquinolines and indigo-blue (p. 417). The formulæ below are those of some of the nitrogen derivatives, in which indole and isoindole may be considered as derived from indene (p. 385): carbazole from fluorene; quinoline, isoquinoline and naphthydrine from naphthalene: acridine and the anthrapyridines from anthracene; and phenanthridine from phenanthrene:



 β -Anthrapyridine.

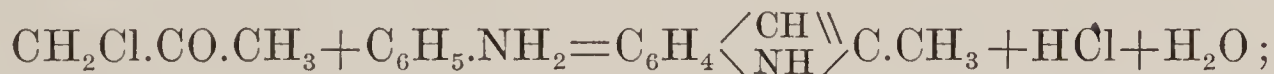
Phenanthridine.

CONDENSED NUCLEI CONTAINING A NITROGEN MEMBER.

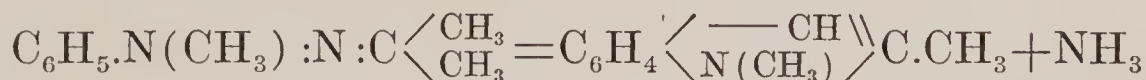
BENZOPYRROLE AND ITS DERIVATIVES—INDIGO COMPOUNDS

Indole—Benzopyrrole—(formula p. 414)—is produced: (1) by distilling oxindole over zinc-dust; (2) by heating o-nitric cinnamic acid with potash and iron filings, or by similar reduction of other unsaturated o-nitro substitution products of benzene (3) by the interaction of calcium formate and phenylglycocoll (p. 375). It is one of the products of putrefaction of the proteins by anerobic bacteria, and is formed in the intestine during pancreatic digestion of those substances. It is partly eliminated with the feces and partly reabsorbed, appearing in the urine in sulphoconjugate combination. It crystallizes in large, shining, colorless plates, having the disagreeable odor of naphthylamine. It is a weak base, and its salts are decomposed by boiling water. Its aqueous solution, acidulated with HCl, is colored rose-red by KNO_2 . By fusion with KOH it yields aniline. It gives the "pine-shaving reaction" (p. 416). It forms a compound, crystallizing in red needles, with picric acid.

Indole Homologues—Derivatives of indole are produced by substitution either in the benzene or in the pyrrole ring. The positions are distinguished as Bz. 1, 2, 3, 4 and Py.*n*, α , and β (see formula p. 414). The alkyl indoles, the superior homologues of indole, are formed: (1) by heating aniline with compounds containing the group $\text{CO}.\text{CH}_2\text{Cl}$. Thus chloracetone and aniline yield α -methyldindole:



(2) By heating the phenylhydrazones of the ketones, aldehydes or ketone acids with ZnCl_2 . Thus *n*, α -dimethyldindole is obtained from acetone-phenyl-methyl-hydrazone:

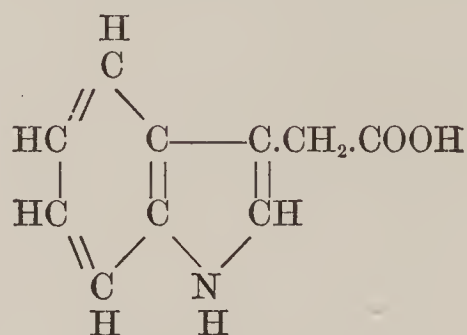


The best known alkyl indoles are those in which the alkyl group is in the pyrrole ring. They dissolve in concentrated acids, and are precipitated unaltered from the solutions by dilution with water. Fused with KOH, they yield potassium salts of indole-carboxylic acids. Their hydrogen may be replaced by acylyls or by the diazo

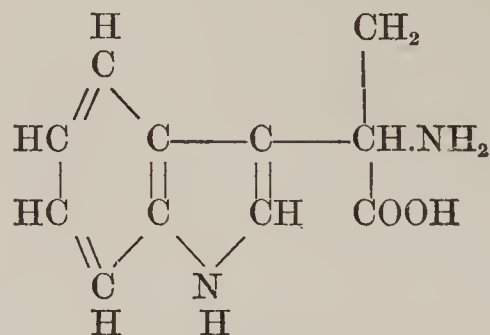
group. They give the "pine-shaving reaction," and form red, crystalline compounds with picric acid.

Indole- β -acetic acid.—The product of putrefaction, which also exists in normal urine, described as skatole carboxylic acid, is not that substance, but its isomere, indole- β -acetic acid (formula below). It produces an intense violet color with HCl and dilute FeCl_3 solution.

Tryptophane—*Proteinochromogen*— **β,β -Indole- α -amidopropionic Acid**—



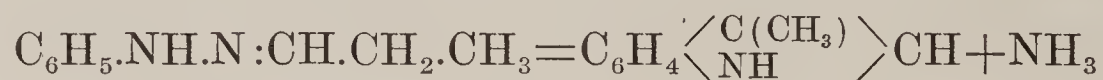
Indole- β -acetic acid.



Tryptophane.

is a product of decomposition of proteins by energetic decomposing agents such as $\text{Ba}(\text{OH})_2$, H_2SO_4 , tryptic digestion and putrefaction, but not by peptic digestion. With Br or Cl it forms a red-violet pigment, called **proteinochrome**. It crystallizes in shining plates, easily soluble in hot water, difficultly in cold water or alcohol. When heated it yields indole and skatole. It gives the Adamkiewicz reaction. Its solution on a pine shaving, previously moistened with HCl, and subsequently washed and dried, gives a purple color (pyrrole reaction). By anerobic putrefaction it yields indole- β -propionic acid; and by aerobic putrefaction indole- β -acetic acid, and indole.

β -Methyl-indole—**Skatole**— $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{C}(\text{CH}_3) \\ \diagdown \text{NH} \end{smallmatrix} \text{CH}$ —exists in feces, in which it exceeds the indole in amount. It is formed during putrefaction of the proteins, or by the action upon them of KOH in fusion; also by the reduction of indigo. It is best obtained synthetically by heating propidene-phenylhydrazone with zine chloride:

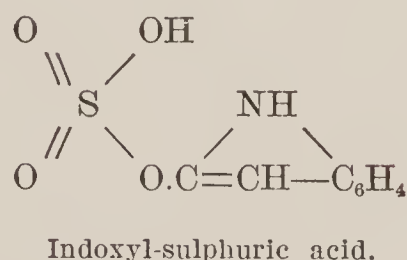
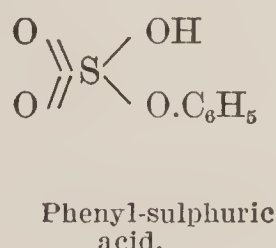
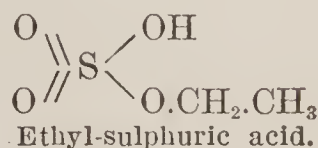
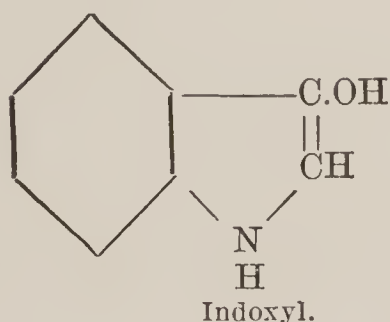
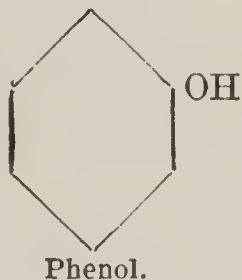
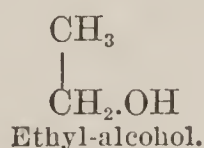


It crystallizes in brilliant plates; f. p. 95° ; insoluble in water, soluble in alcohol and in ether; distils with vapor of water; has a strong fecal odor. Its solution in concentrated HCl is violet. Its H_2SO_4 solution is colored deep purple when heated. Skatole, like indole, is in part reabsorbed from the intestine, and appears in the urine, combined with sulphuric and glucuronic acids.

Iso-indole—(formula, p. 414)—is formed by the action of alcoholic ammonia upon brom-acetophenone. It crystallizes in colorless, silky plates; f. p. 195° ; insoluble in water, soluble in alcohol, ether and benzene.

Indoxyl— **β -Oxyindole**— $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{C}(\text{OH}) \\ \diagdown \text{NH} \end{smallmatrix} \text{CH}$ —not to be con-

founded with oxindole (below), is a phenolic derivative of indole, obtained from indigo-blue by fusion with KOH without contact of air; or from its α -carboxylic acid, **indoxylic acid**. It is a very unstable, oily substance, soluble in water, and readily oxidized to indigo-blue (below). It readily combines with sulphuric acid or the sulphates to form **indoxyl-sulphuric acid**, the potassium salt of which is **uroxanthine**, or **urinary indican**. This latter is formed from indole, and its relations are shown by the following formulæ:



Acids decompose it, with formation of indoxyl, which is converted into indigo-blue by FeCl_3 .

Oxindole— $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}_2 \\ \diagdown \text{NH} \end{smallmatrix} \text{CO}$ —the lactam of o-amido-phenyl acetic acid, is obtained from dioxindole by reduction with sodium amalgam in acid solution; or by reduction of o-nitrophenyl-acetic acid. It crystallizes in easily soluble, colorless needles; f. p. 120° . In moist air it oxidizes to dioxindole. It reduces ammoniacal silver nitrate solution. It combines with acids and bases.

Isatine $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{NH} \end{smallmatrix} \text{CO}$ —the lactam of o-amido-benzoyl-formic acid, is formed by oxidation of indigo-blue by HNO_3 ; by oxidation of oxindole; and by other methods. It crystallizes in shining, transparent, red-brown prisms, odorless, sparingly soluble in water, readily soluble in alcohol.

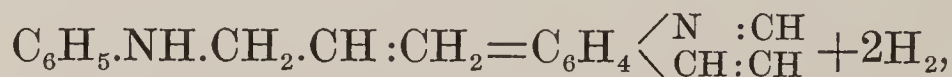
Indigo-blue—Indigotine— $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{NH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$ —constitutes the greater part of commercial indigo. It does not exist preformed in nature, but many plants, particularly *Indigotifera tinctoria* and *Isatis tinctoria*, contain a yellow glucoside, indican (p. 363), which on heating with dilute acids, or probably by enzymic action on exposure to air in presence of water, is decomposed into a sugar and indigo-blue. Commercial indigo contains 20 to 90 per cent. of

indigo-blue, which may be separated, nearly pure, by cautious sublimation. It is formed in several reactions, *e.g.*, by oxidation of indoxyl by FeCl_3 and HCl ; from *o*-nitro-cinnamic acid by two methods; by fusing phenyl-glycocoll with KOH ; or by heating *o*-nitro-acetophenone with zinc dust. It forms purple-red, metallic shining prisms or plates, odorless, tasteless, neutral, soluble in hot aniline, hot oil of turpentine, and melted paraffin, insoluble in the usual solvents. When heated it is in part converted into a dark-red vapor, and partly decomposed into aniline and other products. In the presence of aqueous alkaline solutions, reducing agents convert indigo-blue into **indigo-white**, or **di-indoxyl**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{C}(\text{OH}) \\ \diagdown \text{NH} \end{smallmatrix} \text{C} - \text{C} - \begin{smallmatrix} \diagdown \text{C}(\text{OH}) \\ \diagup \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, which dissolves in the alkali. This substance absorbs oxygen from the air rapidly, with regeneration of indigo-blue. In absence of air it may be precipitated from its alkaline solution by HCl , as a white, crystalline powder, insoluble in water, but soluble in alcohol and ether, forming yellow solutions. When oxidized, as by warming with dilute HNO_3 , indigo-blue is converted into isatine, whose dilute solutions are also yellow. Hence the decoloration of indigo-blue solution is utilized as a test both for oxidizing (HNO_3) and for reducing (Mulder-Neubauer test for glucose) substances.

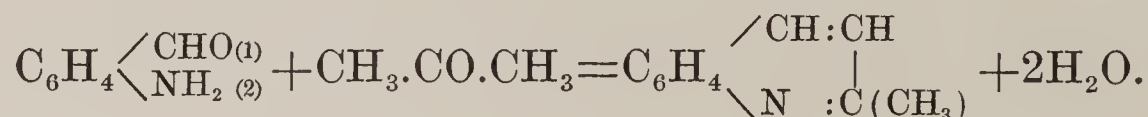
QUINOLINE AND ISO-QUINOLINE AND THEIR DERIVATIVES.

The **quinoline**, or **benzo-pyridine bases** accompany the pyridine bases in bone-oil, and like those substances, are closely related to the vegetable alkaloids. Quinoline, the parent substance of the group, was first obtained by distilling quinine and cinchonine with lime.

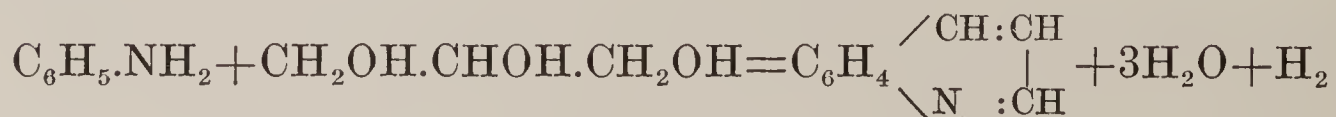
Chemically the quinolines are also related to the naphthalenes, and are formed by similar synthetic methods. Thus quinoline is formed from allyl-aniline:



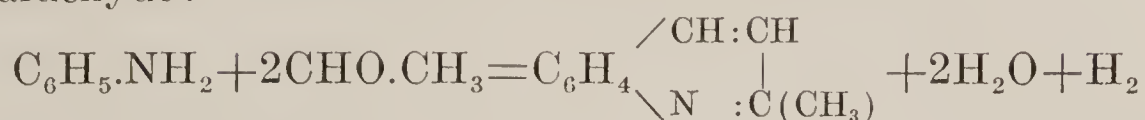
in the same manner as naphthalene is formed from phenyl-butylene. Quinoline and its derivatives may also be produced synthetically: (1) From *o*-amido-benzenic compounds containing an oxygen atom in the second lateral chain. Thus *o*-amido-benzoic aldehyde and acetone yield α -methyl-quinoline:



(2) By heating the anilines with glycerol and H_2SO_4 , in presence of an oxidizing agent, such as nitro-benzene:



(3) By the action of aldehydes upon anilines in presence of H_2SO_4 or HCl . Thus α -methyl-quinoline is obtained from aniline and acetic aldehyde:



The quinoline bases are liquids of penetrating odor, sparingly soluble in water, readily soluble in alcohol and in ether. They are strong triacid bases, and form salts and ammonium-like compounds.

Quinoline— $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH}:\text{CH} \\ \diagdown \text{N} \quad | \\ \quad \text{:CH} \end{array}$ —is a mobile liquid; b. p. 238° , becoming rapidly brown on exposure to air; has an intensely acrid and bitter taste, and an odor somewhat like that of bitter almonds; sparingly soluble in water, readily soluble in alcohol and ether. Its dichromate crystallizes in yellow needles; f. p. 165° ; very sparingly soluble in water.

Quinoline is of medical interest chiefly in connection with the vegetable alkaloids of which it is the nucleus (p. 428). Certain synthetic basic substances containing the quinoline nucleus have also been used in medicine, in saline combination, as antiperiodics and antipyretics.

Iso-quinoline— $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagdown \quad | \\ \text{CH}:\text{N} \end{array}$ —differs from quinoline in that the attachment of the benzene and the pyridine rings is by the β and γ positions of the latter in iso-quinoline, and by the α and β positions in quinoline (see formulæ, p. 414). It accompanies quinoline in coal-tar, and is the nucleus of some of the opium alkaloids (p. 437). It resembles quinoline in its properties. F. p. 23° ; b. p. 240.5° .

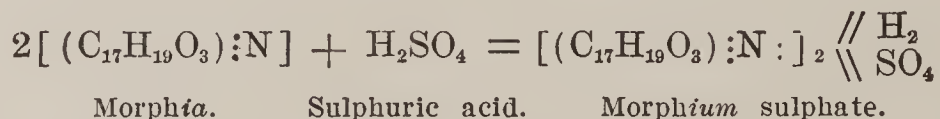
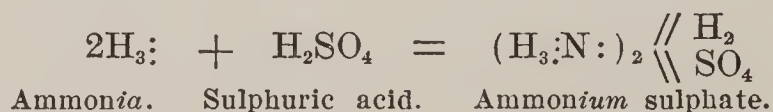
ALKALOIDS.

Until the constitution of all the substances grouped under this term shall have been determined, the limitations of the application of the name can be only provisional. It was first applied to the few alkali-like substances first obtained from vegetable products, the vegetable bases morphine, narcotine, veratrine, strychnine. Afterwards its application was extended, and at the same time made more precise, to include organic, nitrogenized substances, alkaline in reaction, and capable of combining with acids to form salts in the same way as does ammonia. This limitation, is, however, too broad, as it classes the aliphatic amines, and other similar bodies, with the true alkaloids, which are cyclic. All substances generally classed as alkaloids, whose constitution has been determined, contain at least one nitrogen-containing heterocyclic ring, except theobromine and caffeine, which are not true alkaloids, but purine bases (p. 409). Almost all alkaloids of known constitution contain the pyridine ring, more

or less modified by hydrogenation, either alone or in quinoline or isoquinoline. Therefore, until recently, alkaloids were considered to be: basic substances containing the pyridine ring. But the hygrines, alkaloids existing in coca leaves, are derivatives, not of pyridine, but of pyrrolidine, a five-membered nucleus. So far as is now known, no alkaloid contains more than one nitrogen atom in one and the same ring. Therefore, provisionally, it may be stated that the alkaloids are basic substances derived from heterocyclic nuclei containing but one nitrogen atom in any nucleus. Under this definition pyridine and quinoline and their homologues are alkaloids, as well as indole, and other basic pyrrole compounds.

Properties.—Some of the alkaloids, nicotine, coniine, sparteine and arecoline are liquid, volatile, and contain C, N and H. Most of them, to the number of more than a hundred, are solid, crystalline, only partially volatile without decomposition, if at all, and contain C, N, H and O. Most of the alkaloids are very sparingly soluble in water, although some are readily soluble; but soluble in alcohol, ether, petroleum-ether, chloroform, benzene or amyl alcohol. Their salts, on the other hand, are, for the most part, soluble in water, but insoluble in the other solvents mentioned, except alcohol, in which they are soluble. They are laevogyrous, except quinidine, chinchonine, coniine, narcotine, and pilocarpine, which are dextrogyrous. Usually their rotary power is diminished by combination with acids, although with quinine the reverse is the case. Free narcotine is laevogyrous, its salts are dextrogyrous. Most of the alkaloids are bitter in taste, and alkaline in reaction.

The *naming of the salts* of the alkaloids has been the subject of no little discussion. The names of the alkaloids are made to terminate in *ine*. As most of the alkaloids are tertiary amines and some secondary amines, they combine with acids in the same manner that ammonia does, that is, without elimination of water or of hydrogen, and by change of the nitrogen valence from trivalent to quinquivalent:



Therefore these salts do not contain morphine, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}'''$, as a substitute for the hydrogen of the acid, but the hypothetical morphium $(\text{C}_{17}\text{H}_{20}\text{O}_3\text{N}^{\text{v}})'$, as the ammoniacal salts are not salts of ammonia, NH_3 , but of ammonium, NH_4 . The compounds formed by the union of morphine and other alkaloids with the hydracids, HCl , HBr , HI , may properly and conveniently be referred to as morphine hydrochloride (not hydrochlorate) hydrobromide, hydroiodide, etc., they being considered, not as salts of those acids, but as compounds in which one of the valences of the quinquivalent nitrogen atom is satisfied by hydrogen and another by chlorine.

Many of the alkaloids behave like esters, and are hydrolyzed by baryta or the caustic alkalies, or by mineral acids, into two components, one a base, the other an acid, the latter usually cyclic and nitrogenous. On the other hand, concentrated HCl removes H₂O from those alkaloids containing more than one hydroxyl, converting them into apo-alkaloids, as morphine is converted into apomorphine. Other alkaloids, containing methoxyl groups (OCH₃), when acted upon by concentrated HCl, are modified by replacement of OH for the methoxyl groups. Reducing agents with alkaloids whose nuclei contain double bonds, form hydro-bases, as piperidine is derived from pyridine. Distillation with zinc-dust causes removal of the lateral chains from the oxygen-containing alkaloids, with liberation of pyridine or quinoline. Oxidizing agents form carboxylic acids, or decompose the alkaloid into an acid and a base, or cause the union of two molecules of the alkaloid with loss of hydrogen.

General Reactions of the Alkaloids.—A great number of “general reagents” for alkaloids have been suggested, of which only the more important can be here mentioned:

Potash, soda, ammonia, lime, baryta and *magnesia* precipitate the alkaloids from solutions of their salts.

Phosphomolybdic acid forms a precipitate which is bright-yellow with aniline, morphine, veratrine, aconitine, emetine, atropine, hyoscyamine, theïne, theobromine, coniïne, and nicotine; brownish-yellow with narcotine, codeïne, and piperine; yellowish-white with quinine, cinchonine, and strychnine; yolk-yellow with brucine (DeVry's, or Sonnenschein's reagent).

Potassium iodhydrargyrate gives a yellowish precipitate with alkaloidal solutions which are acid, neutral or faintly alkaline in reaction (Mayer's reagent).

Classification of the Alkaloids.—The alkaloids of known, or partially known constitution, can be classified according to the nuclei which they contain:

A. *Pyrrolidine-Alkaloids*.—The hygrines.

B. *Pyridine-Alkaloids*.—Trigonelline, pilocarpine (?).

C. *Piperideïne (tetrahydropyridine) Alkaloids*.—Arecoline, arecäidine γ -coniceïne (?), pseudopelletierine, pelletierine (?).

D. *Piperidine Alkaloids*.—Coniïne, conhydrine, arecäïne, juvacine, piperine.

E. *Pyrrolidine-pyridine Alkaloids*.—Nicotine.

F. *Pyrrolidine-piperidine Alkaloids*.—*Tropan Alkaloids*.—Atropine, hyoscyamine, hyoscine (?), ecgonine, cocaïne, cinnamyl-cocaïne, α -truxilline, β -truxilline, benzoyl-ecgonine, tropacocaïne.

G. *Quinoline Alkaloids*.—Cinchona alkaloids, strychnos alkaloids (?).

H. *Isoquinoline Alkaloids*.—Papaverine, narcotine, narceïne (?), hydrastine, berberine (?).

I. *Phenanthrene Alkaloids*.—Morphine, codeïne, thebaïne.

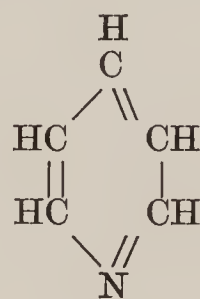
X. Alkaloids of unknown constitution.

Piperidine Alkaloids.—The alkaloids known to contain a single piperidine ring as a nucleus are the five alkaloids of *Conium maculatum*, **coniine**, $C_8H_{17}N$, **conhydrine**, $C_8H_{17}NO$, **coniceine**, $C_8H_{15}N$, ***n*-methyl-coniine**, $C_9H_{19}N$, and **pseudoconhydrine**, $C_8H_{17}NO$; and two of the four betel-nut alkaloids: **arecaine**, $C_7H_{11}NO_2$, and **guvacine**, $C_6H_9NO_2$.

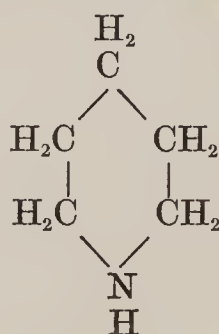
Coniine— $C_8H_{17}N$ —is one of the most simply constituted of the natural vegetable alkaloids, and was the first to be produced synthetically. It is a colorless, oily liquid; has an acrid taste and a disagreeable, penetrating odor; sp. gr. 0.844; can be distilled when protected from air; b. p. 166° . Exposed to air it resinifies. The natural alkaloid is *d*-coniine, $[\alpha]_D = 15.7^\circ$. It is very sparingly soluble in water, but is more soluble in cold than in hot water; soluble in all proportions in alcohol, easily soluble in ether, and in fixed and volatile oils.

Its vapor at ordinary temperatures forms a white cloud when in contact with a glass rod moistened with HCl , as does NH_3 . It forms salts which crystallize with difficulty. Chlorine and bromine combine with it to form crystallizable compounds; iodine in alcoholic solution forms a brown precipitate in alcoholic solutions of coniine, which is soluble without color in an excess. Ethyl and methyl iodides combine with it to form crystallizable compounds; iodine in alcoholic solution forms a brown precipitate in alcoholic solutions of coniine, which is soluble without color in an excess. Ethyl and methyl iodides combine with it to form ethyl- and methyl-coniine hydriodides.

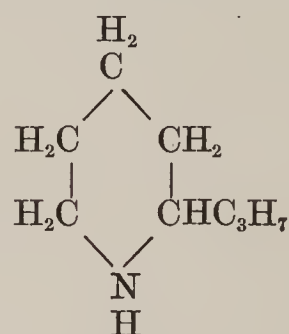
It has been obtained synthetically from α -picoline by reactions which show it to be α -propyl piperidine. The relations of pyridine, piperidine, and coniine are shown by the following formulæ:



Pyridine.



Piperidine.

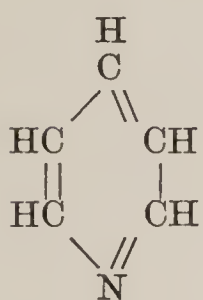


Coniine.

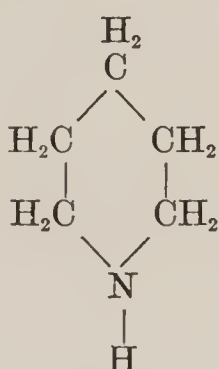
ANALYTICAL CHARACTERS—(1) With dry HCl gas it turns red-dish-purple, and then dark-blue. (2) Aqueous HCl of sp. gr. 1.12 evaporated from coniine leaves a green-blue, crystalline mass. (3) With iodic acid: a white ppt. from alcoholic solutions. (4) With H_2SO_4 and evaporation of the acid: a red color, changing to green, and an odor of butyric acid. (5) When mixed with commercial nitrobenzene a fine blue color is produced, changing to red and yellow.

Paraconiine— $C_8H_{15}N$ —is a synthetical product closely resembling coniine, obtained by first allowing butyric aldehyde and an alcoholic solution of ammonia to remain some months in contact at 30° , when dibutyraldine is formed: $2(C_4H_8O) + NH_3 = C_8H_{17}NO + H_2O$. The dibutyraldine thus obtained is then heated under pressure to 150° – 180° , when it loses water, and forms paraconiine: $C_8H_{17}NO = C_8H_{15}N + H_2O$. A synthesis which, in connection with the decompositions of paraconiine, shows its rational formula to be $(\overset{H}{C_4H_7})'_2 \searrow N$.

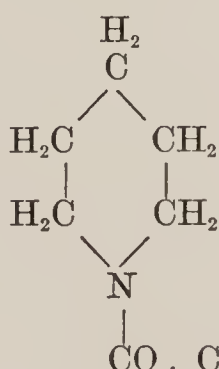
Piperine— $C_{17}H_{19}NO_3$ —isomeric with morphine, and occurring in black and white pepper, crystallizes in large prisms; f. p. 128° ; almost insoluble in water, readily soluble in alcohol and in ether. It is a weak base, without alkaline reaction, and only forming very unstable salts with concentrated acids. It is one of the alkaloids whose complete synthesis has been accomplished, and is quite directly derived from piperidine, of which it is an *n*-acidyl derivative. When piperine is heated with alcoholic soda, it is hydrolyzed into piperic acid, $C_{12}H_{10}O_4$, and piperidine. It is therefore **piperidine piperate**, or **piperidine-3, 4-methylene-dioxy-cinnamyl-acrylate**:



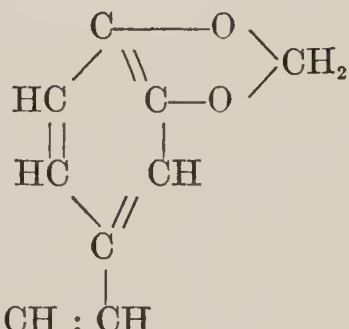
Pyridine.



Piperidine.



Piperine.

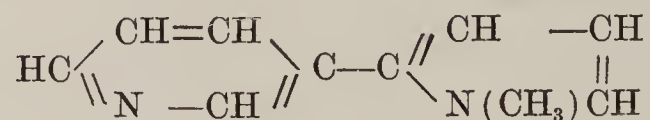


Pyrrolidine-pyridine Alkaloids are represented by

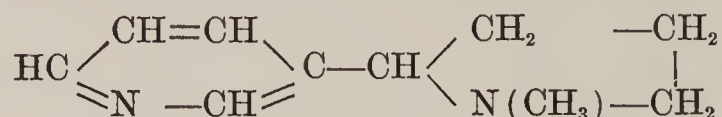
Nicotine— $C_{10}H_{14}N_2$ —which exists in tobacco in the proportion of 2-8 per cent. It is a colorless, oily liquid, which turns brown on exposure to air, has a burning, caustic taste, and a disagreeable, penetrating odor. It distils at 250° ; burns with a luminous flame; sp. gr. 1.027 at 15° ; is very soluble in water, alcohol, the fatty oils, and ether. The last-named fluid removes it from its aqueous solution when the two are shaken together. It absorbs water rapidly from moist air. Its salts are deliquescent, and crystallize with difficulty. The natural alkaloid is l-nicotine. The i-nicotine has been obtained by total synthesis, through β -amidopyridine. From this l-nicotine is produced by the action of tartaric acid.

The oxidation of nicotine produces nicotinic, or β monocarboxypyridic, acid. When distilled with zinc chloride and lime it yields pyrrole, ammonia, methylamine, hydrogen, and pyridine bases. When heated to 250° it yields a collidine along with other products. By limited oxidation it produces a substance, $C_{10}H_{10}N_2$, formerly con-

sidered as isodipyridine, but shown to be β -pyridine-*n*-methyl- α -pyrrole,



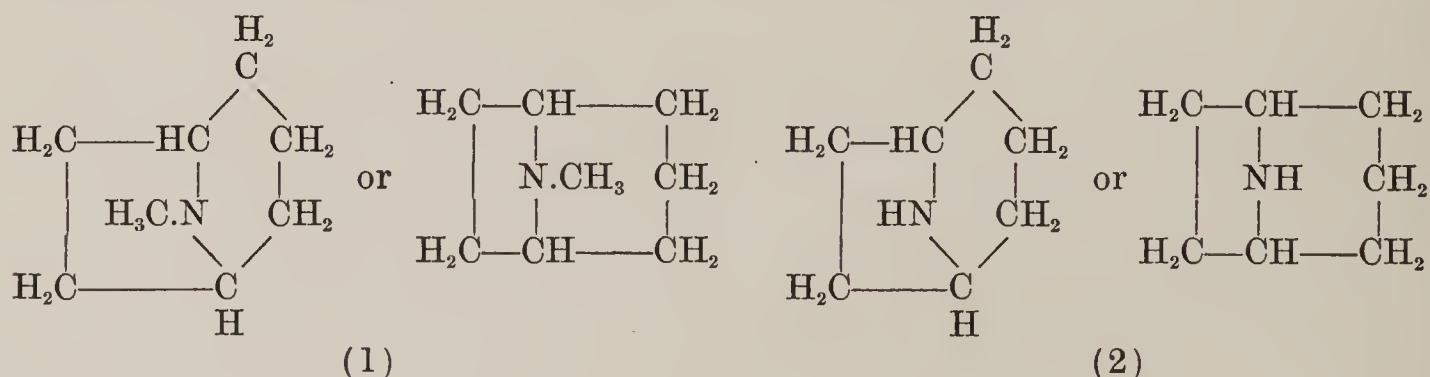
of which nicotine is the tetrahydro, or pyrrolidine derivative—



ANALYTICAL CHARACTERS.—(1) Its ethereal solution, added to an ethereal solution of iodine, separates a reddish-brown, resinoid oil, which gradually becomes crystalline. (2) With HCl, a violet color. (3) With HNO₃, an orange color.

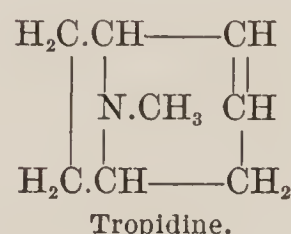
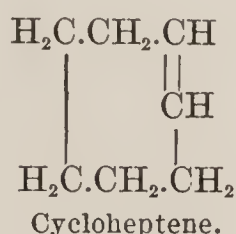
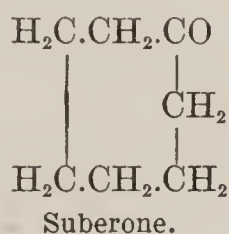
TOXICOLOGY.—Nicotine is a very active poison. The free alkaloid is probably capable of causing death in doses of two to three drops. It was the first alkaloid to be separated from the cadaver in a case of homicide. Most cases of poisoning from nicotine are due to tobacco, frequently resulting from its use in enemata. When administered to dogs in doses of two to four drops, its effects begin within half a minute to two minutes, and death ensues within one to five minutes. In man tobacco or its decoction causes nausea, vertigo, dilatation of the pupils, vomiting, syncope, diminution of the rapidity and force of the heart. With large doses there are no subjective symptoms, the victim falls unconscious instantly, and dies within five minutes, without convulsions, and with very few or only one deep sighing respiratory act. The l-nicotine has double the toxic power of d-nicotine, and the two forms differ in the nature of the action produced.

Pyrrolidine-piperidine Alkaloids—Tropan Alkaloids.—The alkaloids of this group, most of which are ester-alkaloids, including the atropic alkaloids, atropine, hyoscyamine, and hyoscine, and the coca alkaloids, ecgonine, cocaine, cinnamyl-cocaine, α - and β -truxillines, benzoylecgonine and tropacocaine, are derivatives of tropan (1), the *n*-methyl derivative of nortropan (2), both of which are known, as well as many of their compounds other than alkaloids:



Nortropan may be considered as formed by condensation of a pyrrolidine ring and a piperidine ring, having the group =CH.NH.CH= in common. The following tropan derivatives are of interest in connection with the syntheses of atropic and coca alkaloids.

Tropidine—(formula below)—is a dehydrotropan, first obtained as a product of decomposition of atropine, and later of cocaine, thus indicating the relationship of the two alkaloids. It has been obtained by total synthesis, starting from synthetic glycerol (p. 223), through allyl bromide, trimethylene bromide, trimethylene cyanide, glutaric acid (p. 259), to suberone (formula below). From suberone to tropidine many steps are required, the principal intermediate products being cycloheptene (2), cycloheptatriene, and α -methyltropidine:



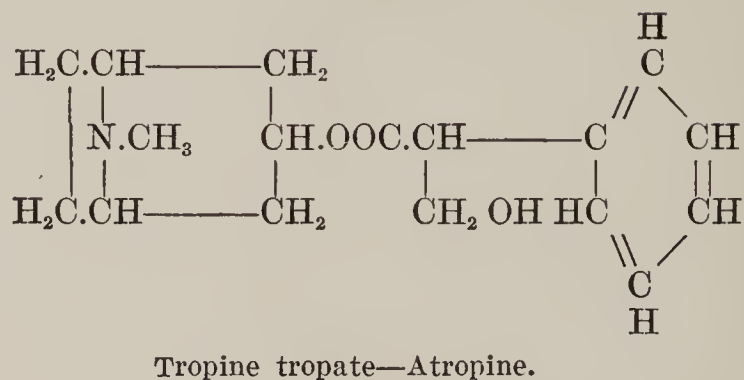
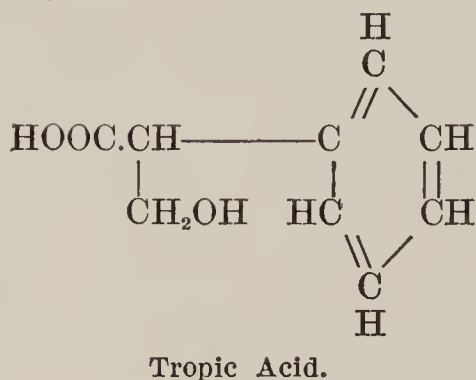
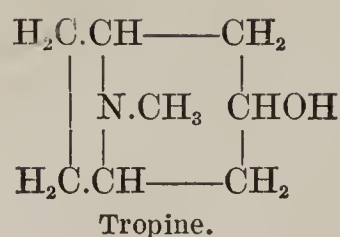
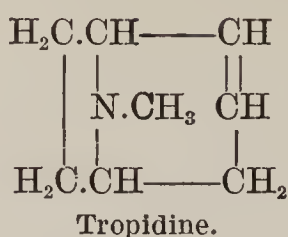
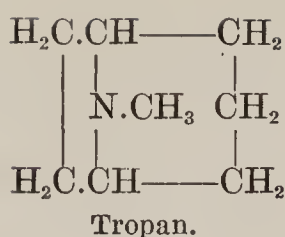
Tropine—(formula p. 426) — **4-Tropan Alcohol** — is formed through its space isomere, Ψ -tropine, by conversion of tropidine into a dibromo addition product, and splitting off of Br_2 and addition of H_2O by heating with H_2SO_4 at 200° . Tropine is the alcoholic component of atropine, hyoscyamine and the tropeïnes, and of which eegonine (p. 427) is the carboxylic acid.

Atropine—i-Tropine tropate— $\text{C}_{17}\text{H}_{23}\text{NO}_3$.—Belladonna, stramonium, hyosyamus and duboisia contain five alkaloids: atropine, hyoscyamine, hyoscine, scopolamine and belladonnine, of which the first two are optical isomeres of each other.

Atropine forms colorless, silky needles, sparingly soluble in cold water, more readily in hot water, very soluble in chloroform. It is odorless, has a disagreeable, persistent, bitter taste. Both tropine and tropic acid (see below) contain an asymmetric carbon atom. The tropine in atropine is i-tropine, and the acid is d-tropic acid. Both natural and synthetic atropines are optically inactive. Atropine is distinctly alkaline, and neutralizes acids with formation of salts. The sulphate is a white, crystalline powder, readily soluble in water.

Atropine is the type of the "ester alkaloids" saponifiable into an acid and an alcoholic component. When it is acted upon by $\text{Ba}(\text{OH})_2$ at 60° , or by NaOH or HCl at 120° – 130° , it is saponified, after the manner of an ester, into tropic, or α -phenylhydracrylic acid, $\text{C}_6\text{H}_5.\text{CH} \begin{smallmatrix} \text{COOH} \\ \text{CH}_2\text{OH} \end{smallmatrix}$, and a secondary cyclic alcohol, tropine (formula below). But if the action be prolonged the tropic acid is further decomposed into α -phenylacrylic, or atropic, and isatropic acids. And if, during the action of HCl , the temperature rises to 180° , the tropine loses water, and is converted into tropidine.

The relation of atropine to its progenitors is shown in the following formulæ:



ANALYTICAL CHARACTERS.—(1) If a fragment of potassium dichromate is dissolved in a few drops of H_2SO_4 , the mixture warmed, a fragment of atropine and a drop or two of H_2O added, and the mixture stirred, an odor of orange-blossoms is developed. (2) A solution of atropine dropped upon the eye of a cat produces dilatation of the pupil. (3) The dry alkaloid (or salt) is moistened with fuming HNO_3 and the mixture dried on the water-bath. When cold, it is moistened with an alcoholic solution of KOH ; a violet color, which changes to red (Vitali). (4) If a saturated solution of Br in HBr is added to a solution of atropine, a yellow precipitate is formed, which rapidly becomes crystalline, and which is insoluble in acetic acid, sparingly soluble in H_2SO_4 and HCl .

TOXICOLOGY.—The clinical history of atropic poisoning is divisible into two stages, the first one of delirium, in which the prominent *symptoms* are dryness of the throat, thirst, difficulty of deglutition and spasms upon swallowing liquids, face at first pale, afterwards highly reddened, pulse extremely rapid, eyes prominent, brilliant, with widely-dilated pupils, complete paralysis of accommodation, disturbances of vision, attacks of giddiness and vertigo, with severe headache, followed by delirium, occasionally silent or muttering, but usually violent, noisy and destructive, accompanied by the most fantastic delusions and hallucinations. Usually the urine is retained, and the body temperature is above the normal. The delirium gradually subsides, and the second stage, that of coma, is established, with slow, stertorous respiration, and gradually failing pulse, until death occurs from respiratory or cardiac paralysis, or sometimes in an attack of syncope during apparent amelioration. In some cases, the patient rapidly becomes comatose at the outset, and the symptoms of the first stage are manifested as the coma diminishes. The *treatment* should consist of lavage of the stomach, and morphine may be given cautiously during the period of violent excitement. In the second stage, the treatment is the same as in morphine poisoning. Pilocarpine may be given, in not too large doses, to stimulate the secretion of saliva. Atropic poisoning leaves no characteristic post-mortem lesions.

Hyoscyamine— $\text{C}_{17}\text{H}_{23}\text{NO}_3$ —isomeric with atropine, predominates in *Hyoscyamus niger*, and in *mandragora*. It differs from atropine

principally in being lævogyrous, $[\alpha]_D = -20.3^\circ$, and on saponification it yields l-tropic acid and i-tropine. It is converted into atropine very easily, by heat, or by addition of alkali to its alcoholic solution.

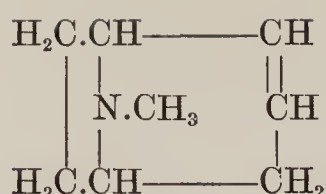
Apoatropine—*Atropamine* — **Tropine atropate** — $C_{17}H_{21}NO_2$ —is formed by the action of dehydrating agents, H_2SO_4 , P_2O_5 , etc., on atropine or hyoscyamine, by splitting off of H_2O from the acid component, thus converting the residue of the saturated tropic acid into that of the unsaturated atropic acid. By heat it is converted into its isomere, **belladonnine**, an alkaloid which accompanies atropine in belladonna. **Hyoscine** and **scopolamine**, $C_{17}H_{21}O_4$, are two isomeric, mydriatic alkaloids, accompanying atropine in belladonna. The latter on decomposition yields tropic acid and **scopoline**, $C_8H_{13}NO_2$, which is closely related to tropine, $C_8H_{15}NO$.

Tropeïnes—are ester-like derivatives of tropine with acids, similar to atropine. Many such have been formed with organic acids, benzoic, salicylic, etc. That formed with mandelic acid is known as **homatropine**, $C_8H_{14}N.OOC.CH(OH).C_6H_5$, is used as a mydriatic having a less prolonged action than atropine. Only those tropeïnes whose acid radicals contain an alcoholic hydroxyl have a mydriatic action.

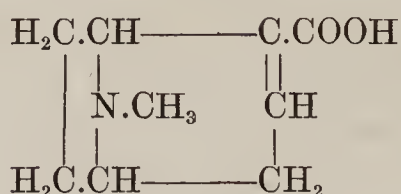
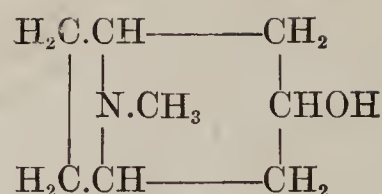
Ecgonine— $C_9H_{15}NO_3$ —an alkaloid existing in *Erythroxylon coca*, and the parent substance of cocaine and other coca alkaloids, is 4-oxytropan-5-monocarboxylic acid (p. 428). By the action of dehydrating agents upon ecgonine the alcoholic OH and an H atom are split off, and **anhydroecgonine**, $C_9H_{13}NO_2$, is formed, which, by splitting off of CO_2 from the carboxyl, forms tropidine. Ecgonine, being both basic and acid, forms esters and salts, and numerous products of derivation other than cocaine. When acted upon by a mixture of methyl iodide and benzoic anhydride, ecgonine is converted into cocaine. Or by substitution of other alkyl iodides for that of methyl, other alkaloids, homologous with cocaine, are obtained (see formulæ below).

Cocaine— $C_{17}H_{21}NO_4$ —the most important of the coca alkaloids, is closely related chemically to atropine. It crystallizes in large four- or six-sided prisms; f. p. 98° ; sparingly soluble in water, readily soluble in alcohol, ether and chloroform; somewhat bitter at first, but causing paralysis of the sense of taste afterwards; strongly alkaline. Its hydrochloride, used as a local anesthetic, crystallizes in prismatic needles, readily soluble in water.

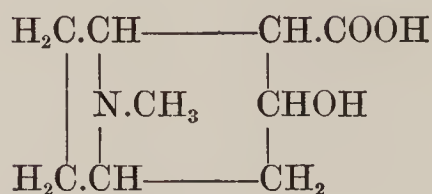
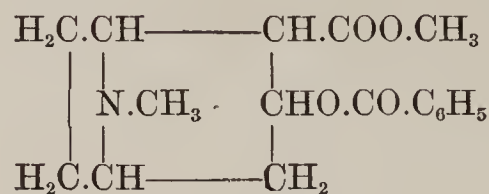
When boiled with water, cocaine is hydrolyzed into **benzoylecgonine**, $C_{16}H_{19}NO_4$, and methylic alcohol. If the hydrolysis is effected by $Ba(OH)_2$, or by concentrated mineral acids, it is more complete, and ecgonine, benzoic acid and methylic alcohol are formed. Cocaine is, therefore, the methyl ester of benzoylecgonine, and ecgonine is tropine-5-monocarboxylic acid:



Tropidine.

Anhydroecgonine.
Tropidine-5-carboxylic acid.

Tropine.

Ecgonine.
Tropine-5-carboxylic acid.Cocaine.
Methyl benzoylecgonate.

ANALYTICAL CHARACTERS.—(1) Picric acid forms a yellow ppt. in concentrated solutions. (2) A solution of iodine in KI solution gives a fine red precipitate in a solution containing 1 to 10,000 of cocaine. (3) When cocaine hydrochloride is heated with concentrated H_2SO_4 until white fumes are given off abundantly, and potassium iodate is added to the still hot liquid, abundant violet vapors are given off, and the liquid becomes deep red-violet, changing to brilliant green, then to pink, and finally to pure blue-violet. (4) Potassium permanganate produces a violet, crystalline ppt. (5) A 5 per cent. solution of chromic acid produces an orange-colored ppt., which immediately redissolves, but, after addition of HCl , remains permanent. (6) If cocaine hydrochloride is mixed dry with HgCl_2 , the white mixture in moist air turns gray or black. Pilocarpine gives the same reaction.

Pilocarpine— $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$ —occurs in jaborandi, along with two other alkaloids, **jaborine**, $\text{C}_{22}\text{H}_{32}\text{N}_4\text{O}_4(?)$, and **pilocarpidine**, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$, and an essential oil, consisting principally of **pilocarpene**, $\text{C}_{10}\text{H}_{16}$. It is colorless, crystalline, readily soluble in water, alcohol, ether and chloroform. It is converted by heat into jaborine; and by HNO_3 or HCl into a mixture of jaborine and **jaborandine**, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$. Like piperine, atropine, cocaine, etc., it is ethereal in character and is decomposed into CO_2 , methylamine, butyric acid, and pyridine bases by KOH or NaOH . When oxidized by potassium permanganate it yields **pyridine-tartronic acid**, $\text{C}_6\text{H}_4\text{N}:\text{C}:(\text{OH})-(\text{COOH})_2$, and this, on further oxidation, nicotinic acid, $\text{C}_5\text{H}_4\text{N}.\text{COOH}$. When its hydrochloride is heated to 200° , in presence of H_2O , it takes up water and is decomposed into pilocarpidine and methylic alcohol. Conversely, pilocarpine is produced by the action of methyl iodide upon pilocarpidine. Although the constitution of pilocarpine is not established, the above and other reactions indicate that it contains the pyridine ring, to which the cyclic group, $\text{C}_6\text{H}_{12}\text{NO}_2$, is attached in the β position; and that it is methyl-pilocarpidine.

Quinoline Alkaloids—Cinchona Alkaloids.—Although by no means so complex a substance as opium, cinchona bark contains a

great number of substances: *quinine*, *cinchonine*, *quinidine*, *cinchonidine*, *aricine*; *quinic*, *quinotannic* and *quinovic acids*; *cinchona-red*, etc. Of these the most important are quinine and cinchonine.

Quinine—Quinina (U. S. P.)— $C_{20}H_{24}N_2O_2 + n \text{ Aq} - 324 + n18$ exists in the bark of a variety of trees of the genera *cinchona* and *China*, which vary considerably in their richness in this alkaloid. The best samples of calisaya bark contain from 30 to 32 parts per 1,000 of the sulphate; the intermediate grades 4 to 20 parts per 1,000; inferior grades of bark contain from mere traces to 6 parts per 1,000.

It is known in three different states of hydration, with 1, 2, and 3 Aq, and anhydrous. The anhydrous form is an amorphous, resinous substance, obtained by evaporation of solutions in anhydrous alcohol or ether. The first hydrate is obtained in crystals by exposing to air recently precipitated and well-washed quinine. The second by precipitating by ammonia a solution of quinine sulphate, in which H has been previously liberated by the action of Zn upon H_2SO_4 ; it is a greenish, resinous body, which loses H_2O at 150° . The third, that to which the following remarks apply, is formed by precipitating solutions of quinine salts with ammonia.

It crystallizes in hexagonal prisms; very bitter; fuses at 57° ; loses 1 Aq at 100° , and the remainder at 125° ; becomes colored, swells up, and, finally, burns with a smoky flame. It does not sublime. It dissolves in 2,200 pts. of cold water, in 763 of hot water, very soluble in alcohol and chloroform; soluble in amyl alcohol, benzene, fatty and essential oils, and ether. Its alcoholic solution is powerfully lævogyrous, $[\alpha]_D = -270.7^\circ$ at 18° , which is diminished by increase of temperature, but increased by the presence of acids.

ANALYTICAL CHARACTERS.—(1) Dilute H_2SO_4 dissolves quinine in colorless but fluorescent solution (see below). (2) Solutions of quinine salts turn green when treated with chlorine-water and then with ammonium hydroxide. (3) Chlorine passed through water holding quinine in suspension forms a red solution. (4) Solution of quinine treated with chlorine-water and then with fragments of potassium ferrocyanide becomes pink, passing to red.

SULPHATE—Quininæ sulphas (U. S. P.)— $(C_{20}H_{24}O_2N_2)_2H_2SO_4 + 7 \text{ Aq} - 746 + 126$ —crystallizes in prismatic needles; very light; intensely bitter; phosphorescent at 100° ; fuses readily; loses its Aq at 120° , turns red, and finally carbonizes; effloresces in air, losing 6 Aq; soluble in 740 pts. of water at 13° , in 30 pts. of boiling water, and 60 pts. of alcohol. Its solution with alcoholic solution of iodine deposits brilliant green crystals of **iodoquinine sulphate**.

HYDROSULPHATE—Quininæ bisulphas (U. S. P.)— $C_{20}H_{24}O_2N_2 \cdot H_2SO_4 + 7 \text{ Aq} - 422 + 126$ —is formed when the sulphate is dissolved in excess of dilute H_2SO_4 . It crystallizes in long, silky needles, or in short, rectangular prisms; soluble in 10 pts. of water at 15° . Its

solutions exhibit a marked fluorescence, being colorless, but showing a fine pale-blue color when illuminated by a bright light against a dark background.

By the action of alkaline hydroxides upon quinine, formic acid, quinoline, and pyridine bases are produced.

Concentrated HCl at 140° – 150° decomposes quinine with separation of methyl chloride and formation of **apoquinine**, $C_{19}H_{22}N_2O_2$, an amorphous base.

Oxidizing agents produce from quinine oxalic acid and pyridine carboxylic acids, notably **pyridine-2 3-dicarboxylic**, or **cinchomeronic acid**, $C_5H_3N(COOH)_2$, which are also formed by oxidation of cinchonine.

Although cinchonine differs from quinine in composition by CH_2O , and although the decompositions of the two bases show them both to be related to the quinoline and pyridine bases, attempts to convert cinchonine into quinine have resulted only in the formation of other products, among which is an isomere of quinine, **oxycinchonine**.

Methylquinine, $C_{20}H_{24}N_2O_2CH_3$, is a base which has a curare-like action.

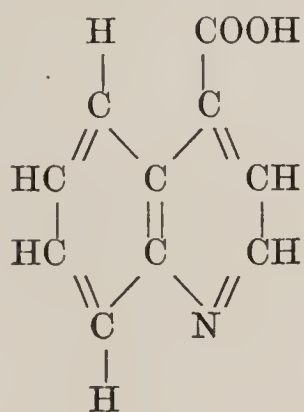
Cinchonine—Cinchonina (U. S. P.)— $C_{19}H_{22}N_2O$ —294—occurs in Peruvian bark to the amount of from 2 to 30 pts. per 1,000. It crystallizes without Aq in colorless prisms; fuses at 150° ; soluble in 3,810 pts. of water at 10° , in 2,500 pts. of boiling water; in 140 parts of alcohol, and in 40 pts. of chloroform. The salts of cinchonine resemble those of quinine in composition; are quite soluble in water and in alcohol; are not fluorescent; are permanent in air; and are phosphorescent at 100° .

Quinidine and Quinicine—are bases isomeric with quinine; the former occurring in cinchona bark, and distinguishable from quinine by its strong dextrorotary power; the second a product of the action of heat on quinine, not existing in cinchona.

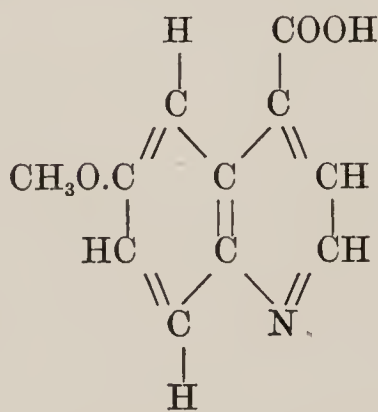
Cinchonidine—a base, isomeric with cinchonine, occurring in certain varieties of bark, lævogyrous. At 130° , H_2SO_4 converts it into another isomere, **cinchonicine**.

Constitution of Cinchona Alkaloids.—The constitution of no cinchona alkaloid has yet been completely determined. Enough has, however, been ascertained to show that cinchonine and quinine contain a quinoline nucleus, united to another cyclic nucleus, containing the second N atom, and which is probably a modified piperidine. The difference between the empirical formulæ of cinchonine, $C_{19}H_{22}N_2O$, and of quinine, $C_{20}H_{24}N_2O_2$, is CH_2O in favor of the latter, which would represent the substitution of methoxyl, CH_3O , for H. When cinchonine and quinine are oxidized by chromic acid they yield two quinoline-carboxylic acids also differing from each other by CH_2O . Cinchonine yields cinchoninic acid, which is known to be γ -quinoline

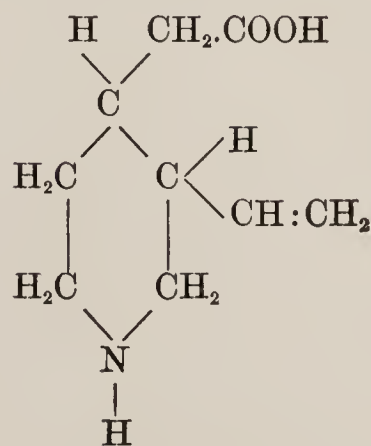
carboxylic acid; while quinine yields quinic acid, which has been shown to be the methyl-phenol ether of p-oxyquinoline- γ -carboxylic acid (see formulæ below). Therefore the group CH_2O , by which cinchonine and quinoline differ, exists in the quinoline ring, and the "second half," or the portion of the molecule other than the quinoline ring, is the same in the two alkaloids. This is further proved by the fact that on decomposition by PCl_5 and subsequent treatment with alcoholic KOH , cinchonine yields lepidine, $\text{C}_{10}\text{H}_9\text{N}$, the next superior homologue of quinoline, $\text{C}_9\text{H}_7\text{N}$, while quinine yields p-methoxy-lepidine, $\text{C}_{10}\text{H}_8(\text{OCH}_3)\text{N}$, and the other product of the decomposition is one and the same substance from either alkaloid, a substance which has been called **meroquinene**, $\text{C}_9\text{H}_{15}\text{NO}_2$, which on treatment with HgCl_2 and HCl is converted into β -ethyl- γ -methyl-pyridine, and whose probable constitution is expressed by the formula given below. So far as determined, therefore, the formulæ of cinchonine and of quinine are those here given, the arrangement of the group $\text{C}_{10}\text{H}_{15}(\text{OH})\text{N}$ remaining to be determined:



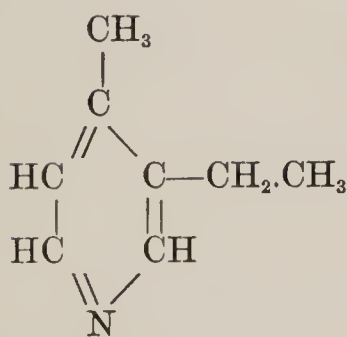
Cinchoninic acid,
(γ -quinoline carboxylic acid).



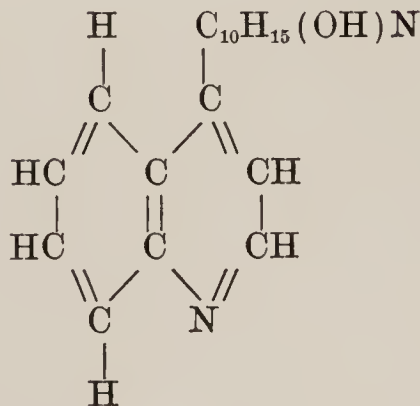
Quinic acid, (3-Methoxyquinoline γ -carboxylic acid).



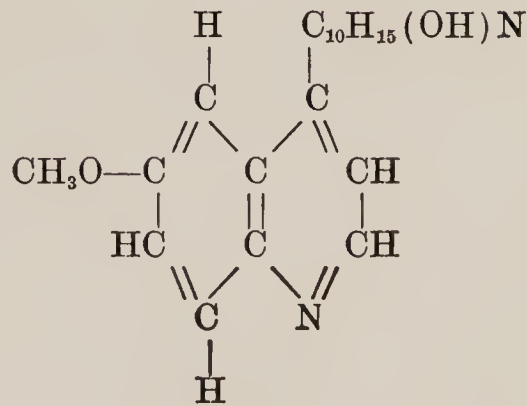
Meroquinene (?)



β -Ethyl- γ -methyl-pyridine.



Cinchonine.



Quinine.

Alkaloids of the Loganiaceæ—Strychnos Alkaloids.—This group includes strychnine and brucine and their alkyl derivatives, and the curare alkaloids.

Strychnine— $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$ —exists in the seeds and bark of different varieties of *Strychnos*, notably *Strychnos nux-vomica*.

It crystallizes on slow evaporation of its solutions in orthorhombic prisms; very sparingly soluble in water and in strong alcohol; soluble

in 5 parts of chloroform. Its aqueous solution is intensely bitter, the taste being perceptible in a solution containing 1 part in 200,000.

It is a powerful base; neutralizes and dissolves in concentrated H_2SO_4 without coloration, and precipitates many metallic oxides from solutions of their salts. Its salts are mostly crystallizable, soluble in water and in alcohol, and intensely bitter. The *acetate* is the most soluble. The *neutral sulphate* crystallizes, with 7 Aq, in rectangular prisms. Methyl and ethyl iodides react with strychnine to produce **methyl** or **ethylstrychnium iodides**, white, crystalline substances, producing an action on the economy similar to that of curare. Heated with fuming HNO_3 , strychnine yields picric acid. Heated with baryta water to 130° , it yields **isostrychnic acid**, $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}.\text{COOH}$; and when treated with sodium alcoholate, **strychnic acid**, by addition of H_2O . By boiling with concentrated hydriodic acid and red phosphorus it is converted into **desoxystrychnine**, $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}$, which is further reduced by electrolysis to **dihydrostrychnoline**, $\text{C}_{21}\text{H}_{28}\text{N}_2$. Strychnine itself, by electrolysis, forms two bases, **tetrahydrostrychnine**, $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2$, and **strychnidine**, $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}$. But little is known of the constitution of strychnine, which is, however, probably a derivative of tetrahydroquinoline.

ANALYTICAL CHARACTERS.—(1) Dissolves in concentrated H_2SO_4 , without color. The solution deposits strychnine when diluted with water, or when neutralized with magnesia or an alkali. (2) If a fragment of potassium dichromate (or other substance capable of yielding nascent oxygen) is drawn through a solution of strychnine in H_2SO_4 , it is followed by a streak of color; at first blue (very transitory and frequently not observed), then a brilliant violet, which slowly passes to rose-pink, and finally to yellow. Reacts with $\frac{1}{50000}$ grain of strychnine. (3) A dilute solution of potassium dichromate forms a yellow, crystalline ppt. in strychnine solutions, which, when washed and treated with concentrated H_2SO_4 , gives the play of colors indicated in 2. (4) If a solution of strychnine is evaporated on a bit of platinum foil, the residue moistened with concentrated H_2SO_4 , the foil connected with the $+$ pole of a single Grove cell, and a platinum wire from the $-$ pole brought in contact with the surface of the acid, a violet color appears upon the surface of the foil. (5) Strychnine and its salts are intensely bitter. (6) A solution of strychnine introduced under the skin of the back of a frog causes difficulty of respiration and tetanic spasms, which are aggravated by the slightest irritation, and twitching of the muscles during the intervals between the convulsions. With a small frog, $\frac{1}{16000}$ grain of strychnine acetate will produce tetanic spasms in ten minutes. White mice, 14 to 16 days old, are even more susceptible to the action of strychnine than frogs. (7) Solid strychnine, moistened with a solution of iodic acid in H_2SO_4 , produces a yellow color, changing to brick-red, and then to violet-red. (8) Moderately concentrated HNO_3 colors strychnine

yellow in the cold. (9) A warm solution of strychnine in dilute HNO_3 produces a scarlet-red color on addition of a little KClO_3 . A drop or two of ammonia changes this to brown. On evaporation to dryness, green residue remains, which forms a green solution in water, changes to orange-brown with KOH , and returns to green with HNO_3 .

TOXICOLOGY.—Strychnine produces a sense of suffocation, thirst, tetanic spasms, usually opisthotonos, sometimes emprosthotonos, occasionally vomiting, contraction of the pupils during the spasms, and death either by asphyxia during a paroxysm, or by exhaustion during a remission. The symptoms appear in from a few minutes to an hour after taking the poison, usually in less than twenty minutes; and death in from five minutes to six hours, usually within two hours. Death has been caused by $\frac{1}{4}$ grain, and recovery has followed the taking of 20 grains.

The treatment should consist in bringing the patient under the influence of chloral hydrate or of chloroform, and then washing out the stomach. The patient should be kept as quiet as possible, as the slightest unexpected irritation will produce a spasm.

Strychnine is one of the most stable of the alkaloids, and may remain for a long time in contact with putrefying organic matter without suffering decomposition.

Brucine— $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4 + 4\text{Aq} - 394 + 72$ — accompanies strychnine. It forms oblique rhomboidal prisms, which lose their Aq in dry air. Sparingly soluble in H_2O , readily soluble in alcohol, chloroform, and amyl alcohol; intensely bitter. It is a powerful base and most of its salts are soluble and crystalline. Its action on the economy is similar to that of strychnine, but much less energetic.

ANALYTICAL CHARACTERS.—(1) Concentrated HNO_3 colors it bright red, soon passing to yellow; stannous chloride, or colorless NH_4HS , changes the red color to violet. (2) Chlorine-water, or Cl , colors brucine bright red, changed to yellowish-brown by NH_4OH .

Curarine— $\text{C}_{36}\text{H}_{35}\text{N}(?)$ —is an alkaloid obtainable from the South American arrow-poison, *curare*, or *woorara*. It crystallizes in four-sided, colorless prisms, which are hygroscopic, faintly alkaline, and intensely bitter.

Curarine dissolves in H_2SO_4 , forming a pale-violet solution, which slowly changes to red. If a crystal of potassium dichromate is drawn through the H_2SO_4 solution, it is followed by a violet coloration, which differs from the similar color obtained with strychnine under similar circumstances, in being more permanent, and in the absence of the following pink and yellow tints.

Isoquinoline and Phenanthrene Alkaloids.—The opium, hydrastis, berberis and corydalis alkaloids are included in these groups. Of the opium alkaloids, papaverine, narcotine and narceine are certainly derivatives of isoquinoline. Morphine and codeine, on the other hand, do not contain the isoquinoline nucleus, but a phenanthrene nucleus having a nitrogen-containing ring condensed upon it. But until the constitution of these two alkaloids is established with more com-

pleteness it is not desirable to separate them from their congeners (see p. 437).

Opium Alkaloids.—Opium is the dried juice obtained by making incisions in the unripe capsules of the poppy, *Papaver somniferum*. It is of exceeding complex composition, and contains meconic, lactic and sulphuric acids, with which the alkaloids are in combination, meconine, gum, caoutchouc, wax, sugar, resins, etc., and a number of alkaloids. Some twenty alkaloids have been obtained from opium, but of these several are probably produced by the processes of extraction. The most important of the natural alkaloids and the average percentage in which they exist in opium of good quality are: morphine, 10%; narcotine, 6%; papaverine, 1%, codeïne, 0.3%; narceïne, 0.2%; and thebaine, 0.15%.

Morphine—Morphina (U. S. P.)— $C_{17}H_{19}NO_3 + Aq - 285 + 18$ —crystallizes in colorless prisms; odorless, but very bitter; it fuses at 120° , losing its Aq. More strongly heated, it swells up, becomes carbonized, and finally burns. It is soluble in 1,000 pts. of cold water, in 400 pts. of boiling water; in 265 pts. of alcohol of 90 per cent. at 10° , and in 33 pts. of boiling alcohol of the same strength; in 373 pts. of cold amyl alcohol, much more soluble in the same liquid warm; almost insoluble in aqueous ether; rather more soluble in alcoholic ether; almost insoluble in benzene; soluble in 2,500 pts. of chloroform at 9° , and in 45 pts. at 56° . All the solvents dissolve morphine more readily and more copiously when it is freshly precipitated from solutions of its salts than when it has become crystalline.

Morphine combines with acids to form crystallizable salts, of which the hydrochloride, sulphate and acetate are used in medicine. If morphine is heated for some hours with excess of HCl, under pressure, to 150° , it loses water, and is converted into a new base—**apomorphine**, $C_{17}H_{17}NO_2$.

By heating together acetic anhydride and morphine, **acetylmorphine**, $C_{17}H_{18}(C_2H_3O)NO_3$, and **diacetylmorphine**, $C_{17}H_{17}(C_2H_3O)_2NO_3$, are formed. The latter is used as a medicine under the name **heroine**. Similarly substituted **butyryl-**, **benzoyl-**, **succinyl-**, **camphoryl-**, **methyl-**, and **ethyl-morphine**, are also known. The last named is used medicinally under the name **dionine**.

Morphine is readily oxidized and a strong reducing agent. It reduces the salts of gold and silver in the cold. It is oxidized by atmospheric oxygen when it is in alkaline solution, as well as by nitrous acid, potassium permanganate, potassium ferricyanide, or ammoniacal cupric sulphate, with the formation of a non-toxic compound which has received the names, **pseudomorphine**, **oxymorphine**, **oxydimorphine**, and **dehydromorphine** $(C_{17}N_{18}NO_3)_2$, whose molecule consists of two morphine molecules, united with loss of H_2 . **Morphine sulphuric acid**, properly **morphylsulphuric acid**, or *monomorphyl sulphate*, $C_{18}H_{18}NO_2.O.SO_3H$, corresponds to ethyl sulphuric acid and phenyl

sulphuric acid, and is obtained by the same method as the latter compound from morphine. It contains H_2O less than morphine sulphate, from which it differs in that the acidyl is attached through a hydroxyl, whereas in the salt it is attached to the nitrogen. When morphine is administered it appears in the urine as pseudomorphine, and also probably as morphylsulphuric acid, both of which are non-toxic. When morphine is distilled with powdered zinc, the principal product of the reaction is phenanthrene, accompanied by ammonia, trimethylamine, pyrrole, pyridine, and a product having the formula $\text{C}_{17}\text{H}_{11}\text{N}$, probably phenanthrene-quinoline.

The salts of morphine are crystalline. The *acetate* is a white crystalline powder, soluble in 12 parts of water, which decomposes on exposure to air, with loss of acetic acid. The *chloride* is less soluble, but more permanent than the acetate. The *sulphate* is the form in which morphine is the most frequently used in medicine. It is a very light, crystalline, feathery powder; odorless, bitter, and neutral in reaction. It dissolves in 24 parts of water. Its solutions deposit morphine as a white precipitate on addition of an alkali. The crystals contain 5 Aq, which they lose at 130° .

ANALYTICAL CHARACTERS.—(1) It is colored orange, changing to yellow, by HNO_3 . (2) A neutral solution of a morphine salt gives a blue color with neutral solution of ferric chloride. (3) A solution of molybdic acid in H_2SO_4 (Fröhde's reagent) gives with morphine a violet color, changing to blue, dirty green, and faint pink. Water discharges the color. (4) Take two test-tubes. Into one (*a*) put the solution of morphine, into the other (*b*) an equal bulk of H_2O . Add to each a granule of iodic acid and agitate; *a* becomes yellow or brown, *b* remains colorless. To each add a small drop of chloroform and agitate: the CHCl_3 in *a* is colored violet, that in *b* remains colorless. Float some very dilute ammonium hydroxide solution on the surface of the liquid in *a*; a brown band is formed at the junction of the layers. (5) Moisten the solid material with HCl to which a small quantity of H_2SO_4 has been added, and heat in an air oven at 110° until HCl is expelled: a violet-colored liquid residue remains. Add to this a drop or two of water containing a little HCl , and neutralize with powdered sodium bicarbonate in slight excess: a pink or rose color is produced, most distinctly visible on the bubbles. Add a drop of water and a drop or two of alcoholic solution of iodine: a green color is developed. This reaction, known as the Pellagri test, is based upon the conversion of morphine into apomorphine, and consequently reacts with that alkaloid. (6) Moisten the solid with concentrated H_2SO_4 , and heat cautiously until white fumes begin to be given off, cool and touch the liquid with a glass rod moistened with dilute HNO_3 : a fine blue-violet color, changing to red and then to orange. If the H_2SO_4 contains oxides of nitrogen, as it usually does, a violet tinge will be pro-

duced before addition of HNO_3 , but then becomes much more intense. This reaction, known as the Husemann, may be applied by allowing the solid to remain in contact with H_2SO_4 for fifteen to eighteen hours in place of heating. (7) Marquis' reagent (3 cc. concentrated $\text{H}_2\text{SO}_4 + 2$ gtt. formaline) gives a brilliant red-violet color. These are the most important tests for morphine, and affirmative results with all of them prove the presence of that alkaloid. There are many others.

Codeine—Codeina (U. S. P.)— $\text{C}_{18}\text{H}_{21}\text{NO}_3 + \text{Aq} - 299 + 18$ —crystallizes in large rhombic prisms, or from ether, without Aq, in octahedra; bitter; soluble in 80 pts. cold water; 17 pts. boiling water; very soluble in alcohol, ether, chloroform, benzene; almost insoluble in petroleum-ether.

Codeine is the methyl ether of morphine, or its superior homologue, and resembles that alkaloid in some of its reactions; thus under similar circumstances both form apomorphine; and morphine may be converted into codeine by the action of methyl iodide in the presence of KOH. Codeine, however, only contains one OH group, and forms a monoacetyl derivative with acetyl chloride, while morphine produces a diacetyl compound.

Narceine — $\text{C}_{23}\text{H}_{27}\text{NO}_8 + 2\text{Aq} - 463 + 36$ — crystallizes in bitter, prismatic needles; sparingly soluble in water, alcohol, and amyl alcohol; insoluble in ether, benzene, and petroleum-ether.

Narcotine— $\text{C}_{22}\text{H}_{23}\text{NO}_7 - 413$ —crystallizes in transparent prisms, almost insoluble in water and in petroleum-ether; soluble in alcohol, ether, benzene, and chloroform. Its salts are mostly uncrystallizable, unstable, and readily soluble in water and in alcohol.

Narcotine is decomposed by H_2O at 140° , by dilute H_2SO_4 , or by baryta, with formation of **opianic acid**, $\text{C}_{10}\text{H}_{10}\text{O}_5$, and **hydrocotarnine**, $\text{C}_{12}\text{H}_{15}\text{NO}_3$. Reducing agents decompose it into hydrocotarnine and **meconine**, $\text{C}_{10}\text{H}_{10}\text{O}_4$. Oxidizing agents convert it into opianic acid and **cotarnine**, $\text{C}_{12}\text{H}_{13}\text{NO}_3$.

Papaverine— $\text{C}_{20}\text{H}_{21}\text{NO}_4$ —crystallizes in prisms; almost insoluble in water, easily soluble in chloroform and in hot alcohol. It is optically inactive. It forms a colorless solution with concentrated H_2SO_4 , which turns dark-violet when heated. Acetic anhydride has no action upon it.

Thebaine—Paramorphine— $\text{C}_{19}\text{H}_{21}\text{NO}_3 - 311$ —crystallizes in white plates; tasteless when pure; insoluble in water, soluble in alcohol, ether and benzene.

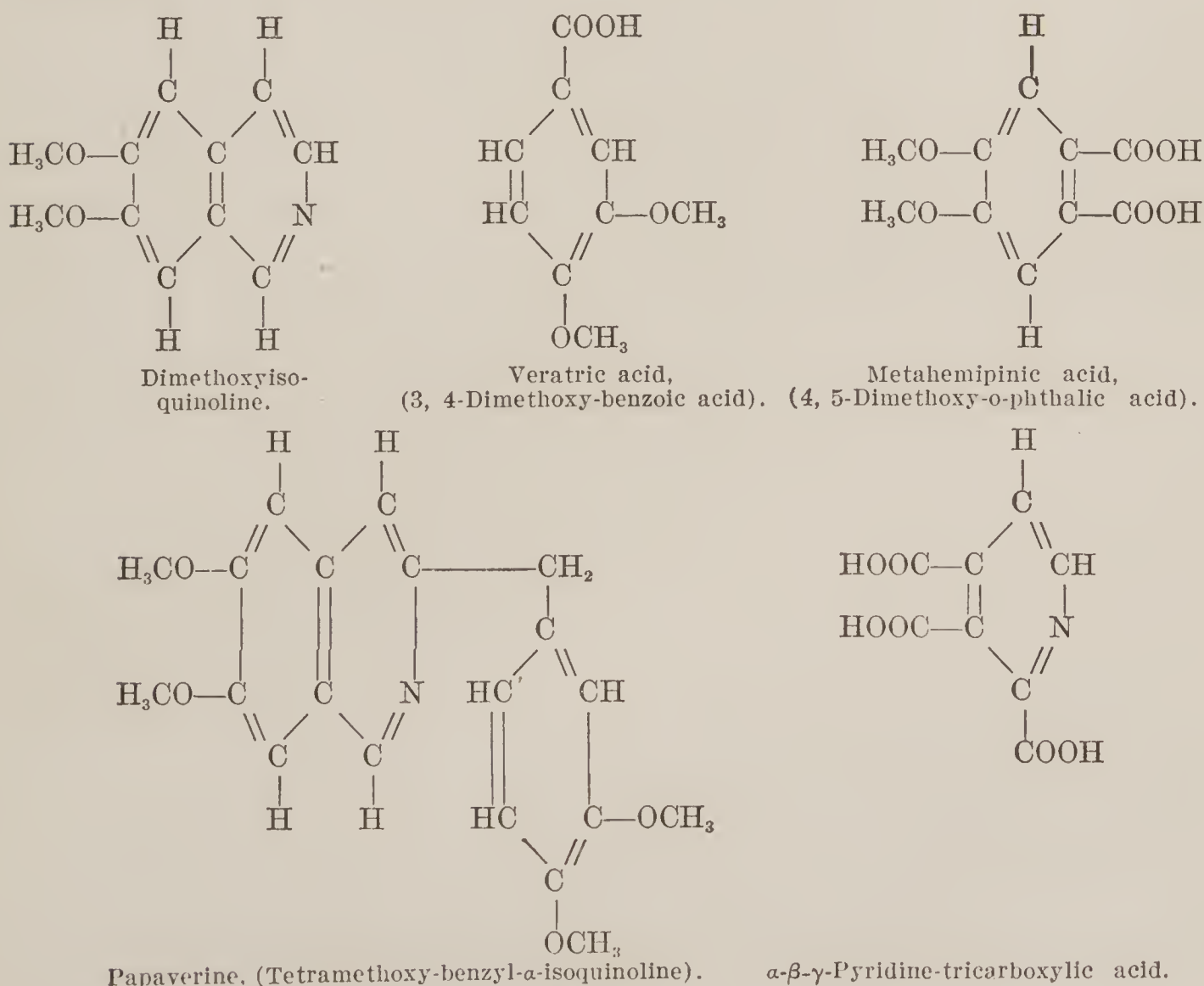
Apomorphine— $\text{C}_{17}\text{H}_{17}\text{NO}_2$ —is used hypodermically as an emetic in the form of the chloride. It is obtained by sealing morphine, with an excess of strong HCl, in a thick glass tube, and heating the whole to 140° for two to three hours. It is obtained also by the same process from codeine. The free alkaloid is a white, amorphous solid, difficultly soluble in water. The chloride forms colorless, shining crystals, which have a tendency to assume a greenish tint on ex-

posure to light and air. It is odorless, bitter and neutral; soluble in 6.8 parts of cold water.

Relations and Constitution of the Opium Alkaloids.—The alkaloids of opium may be arranged in two groups: (I) Including those which are strong bases, are highly poisonous, and contain three or four atoms of oxygen; (II) those which are weak bases and contain four to nine oxygen atoms. So far as known, the alkaloids of the first group contain the phenanthrene-pyridine nucleus, while those of the second group are derivatives of isoquinoline. The six principal alkaloids above mentioned are equally divided between the two groups:

I.		II.	
MorphineC ₁₇ H ₁₉ NO ₃	PapaverineC ₂₀ H ₂₁ NO ₄
CodeineC ₁₈ H ₂₁ NO ₃	NarcotineC ₂₂ H ₂₃ NO ₇
ThebaineC ₁₉ H ₂₁ NO ₃	NarceineC ₂₃ H ₂₇ NO ₈

Papaverine was first recognized as an isoquinoline derivative. On oxidation of papaverine by potassium permanganate, **papaveraldine**, C₂₀H₁₉NO₅, is formed. This, on fusion with caustic potash, yields veratric acid, which is 3, 4-dimethoxy-benzoic acid, C₆H₃.COOH: (OCH₃)₂ (3, 4), and dimethoxyisoquinoline, the constitution of the latter being established by its further decomposition into metahemipinic acid and α - β - γ -pyridine-tricarboxylic acid. The relations of papaverine and its products of decomposition are shown by the following formulæ:

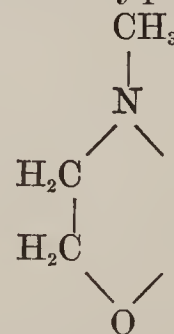


Narcotine, $C_{22}H_{23}NO_7$, is converted by oxidation into opianic acid, $C_{10}H_{10}O_5$ (p. 436), and **cotarnine**, $C_{12}H_{15}NO_4$. By hydrolysis it yields opianic acid and **hydrocotarnine**, $C_{12}H_{15}NO_3$; and by reduction, **mecotine**, $C_{10}H_{10}O_4$ (p. 436), and hydrocotarnine. Narcotine, therefore, contains the nuclei of opianic acid, or of meconine, and of hydrocotarnine. The constitution of opianic acid is known, as well as that of its reduction product, meconine, but that of hydrocotarnine is not completely established. It is, however, a derivative of isoquinoline, containing one of the three methoxy groups (CH_3O) which exist in narcotine, and a bivalent group— $O.CH_2.O$ —attached to the benzene ring; and a methyl group, united to the N atom in the pyridine ring.

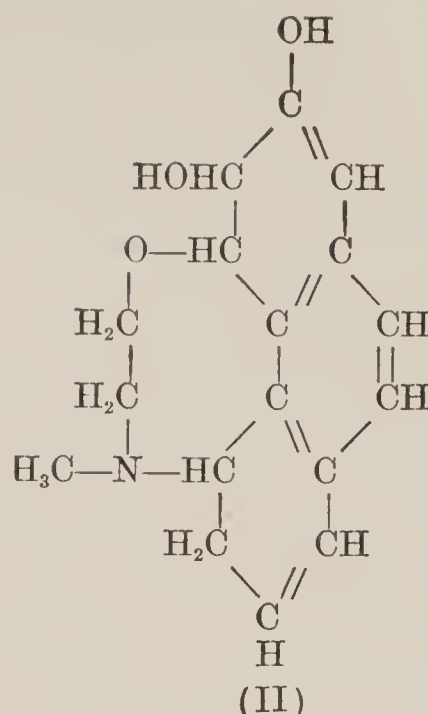
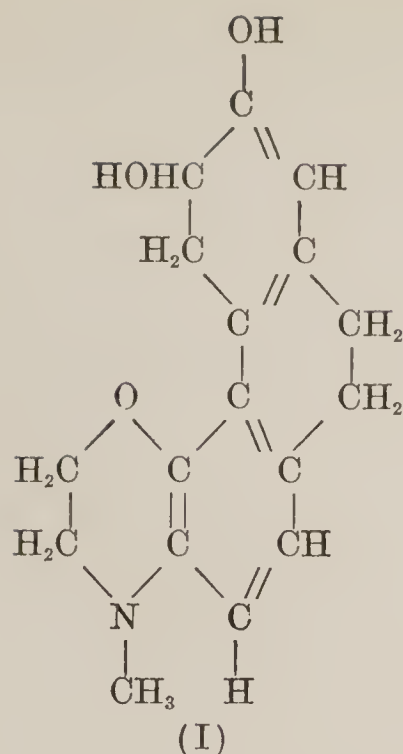
Narceïne, $C_{23}H_{27}NO_8$ is formed by the action of caustic potash upon narcotine iodomethylate: $C_{22}H_{23}NO_7.CH_3I + KOH = KI + C_{23}H_{27}NO_8$. Narceïne apparently does not contain an isoquinoline grouping, that which exists in narcotine having been broken in the above method of formation in such manner that the N is in a lateral chain in narceïne.

Morphine, $C_{17}H_{19}NO_3$, and **codeïne**, $C_{18}H_{21}NO_3$, are closely related. Codeïne is produced by the action of methyl iodide upon morphine-potassium: $C_{17}H_{18}KNO_3 + CH_3I = KI + C_{17}H_{18}(CH_3)NO_3$. It is, therefore, **methyl-morphine**. By the further action of methyl iodide upon codeïne in alcoholic solution, **codeïne methyl iodide**, $C_{18}H_{21}NO_3:CH_3I$, is produced, and this, when warmed with KOH, is converted into **methyl-morphine methine**, $C_{17}H_{19}NO_3:CH.CH_3$. The last-named substance is decomposed by acetic anhydride into methyldioxyphenanthrene and oxethyl-dimethyl-amine: $C_{17}H_{19}NO_3:CH.CH_3 = C_{14}-$

$H_8 \begin{matrix} \diagup OH \\ \diagdown O.CH_3 \end{matrix} + N \begin{matrix} \diagup CH_3 \\ - CH_3 \\ \diagdown CH_2.CH_2.OH \end{matrix}$; and other morphine and codeïne derivatives are similarly decomposed, with formation, on the one hand, of a non-nitrogenized oxy-phenanthrene compound, and, on the other, an oxyamine or a trialkyl-amine. Upon these facts, it is concluded, that the morphine and codeïne molecules consist of an oxyphenanthrene

group, upon which is fused a nitrogenized group, . It is also

recognized that the two hydroxyls are in the same phenanthrene ring, and that one of them is phenolic, the other alcoholic; also that one methyl group is attached to the nitrogen atom. The disposal of the hydrogen and hydroxyls in the phenanthrene nucleus and the position of attachment of the nitrogenized group above referred to remain undetermined. Two formulæ of constitution of morphine have been proposed, either of which is in consonance with the known facts:



The formula of codeine is derived from either formula by substitution of CH_3 for H in the phenolic OH; that of apomorphine by removal of H_2O .

Thebaine, $\text{C}_{19}\text{H}_{21}\text{NO}_3$, is decomposed by acetic anhydride in a manner quite analogous to the decomposition of morphine, above referred to, but yielding a dimethoxy-phenolic derivative of phenanthrene, called **thebaol**, and methyl-oxethyl-amine: $\text{C}_{19}\text{H}_{21}\text{NO}_3 + \text{H}_2\text{O} = (\text{CH}_3\text{O})_2\text{C}_{14}\text{H}_7.\text{OH} + \text{N} \begin{array}{l} \diagup \text{H} \\ - \text{CH}_3 \\ \diagdown \text{CH}_2.\text{CH}_2.\text{OH} \end{array}$. Like morphine and codeine, it is therefore a phenanthrene-pyridine derivative.

Toxicology of Opium and its Derivatives.—Opium, its preparations and the alkaloids obtained from it are all active poisons. The alkaloids have not all the same action. In *soporific effects*, beginning with the most powerful, they rank thus: narcotine, morphine, codeine; in *tetanizing action*: thebaine, papaverine, narcotine, codeine, morphine; in *toxic action*: thebaine, codeine, papaverine, narceine, morphine, narcotine.

The *symptoms* set in from ten minutes to three hours, exceptionally “immediately,” or only after eighteen hours. They are divisible into three periods: (1) a *stage of excitement*, marked by great physical activity, loquacity and imaginative power; is of short duration; longest in opium habitues, absent with large doses; (2) a *period of sopor*, in which there are diminished sensibility, weariness, contracted pupils, pale face, livid lips, drowsiness, increasing to deep sleep, from which, however, the patient may be roused, and when so roused is coherent in speech. This stage merges insensibly into the third, that of *coma*. The patient can no longer be aroused, even by violent means. The face is pale, the lips cyanosed, the muscular system completely relaxed, the reflexes abolished, the pupils contracted greatly, and insensible to light, the pulse slow, irregular, compressible, and finally imperceptible, the respiration more and more infrequent, stertorous, shallow, and accompanied by mucous râles. Retention of urine begins early in the poisoning. The usual duration of a fatal poisoning is from six to twenty-four hours. Deaths have occurred in forty-five minutes and in three days.

The minimum lethal dose for a non-habituated adult is probably 3 to 4 grains. Young children are very susceptible. Tolerance to a remarkable degree

is established by habit, both in children and in adults, and instances are reported in which 50 to 60 grains have been taken daily, without toxic effects, by morphine takers.

The *treatment* should consist in washing out the stomach with a dilute solution of potassium permanganate, leaving about 500 cc. in the stomach, and in maintaining the respiration. In the first or second stage the "ambulatory treatment" should be adopted to prevent, if possible, the establishment of the third stage. If this stage develops, the main reliance is to be placed in maintaining the respiration by artificial methods, until the poison has been eliminated. Strong coffee, or caffeine, by the mouth or rectum are of benefit. The same cannot be said of atropine. The urine should be drawn by the catheter.

The opiates leave no post-mortem lesions, except such as are usually observed after death from asphyxia, *i.e.*, congestion of the vessels of the brain and meninges, and of the lungs, and a dark, fluid condition of the blood.

Alkaloids of unknown constitution.—Of the numerous alkaloids whose constitution is insufficiently known to permit of their classification, only a few can be here briefly considered:

Alkaloids of the Aconites.—The different species of *Aconitum* contain probably a number of alkaloids, but our knowledge of them is as yet extremely imperfect. The substances described as *aconitine*, *lycoctonine*, *napelline* are impure. It appears, however, that the principal alkaloids of *Aconitum napellus* and of *A. ferox*, although differing from each other, are both compounds formed by the union of aconine, $C_{25}H_{41}NO_9$, with the radical benzoic acid in the former and with that of veratric acid in the latter.

Aconitine—Acetylbenzoyl-aconine— $C_{25}H_{39}(CH_3.CO)(C_6H_5.CO)NO_9$ —the principal alkaloid of *A. napellus*, is a crystalline solid, almost insoluble in water, and very bitter. It is decomposed by H_2O at 140° and by KOH into aconine and acetic and benzoic acids. It is very poisonous.

Pseudo-aconitine— $C_{36}H_{49}NO_{12}$ —occurs in *A. ferox*. It is a crystalline solid, having a burning taste, and is extremely poisonous. On decomposition by H_2O at 140° it yields aconine veratric acid.

Japaconitine— $C_{66}H_{88}N_2O_{21}$ —has been obtained from the root of *A. japonicum*, and is a crystalline solid which is decomposed by alkalies into benzoic acid and japaconine, $C_{26}H_{41}NO_{10}$.

The color reactions described as characteristic of "aconitine" are not due to the alkaloid.

Toxicology.—Aconite and "aconitine" have been the agents used in quite a number of homicidal poisonings.

The *symptoms* usually manifest themselves within a few minutes; sometimes are delayed for an hour. There is numbness and tingling, first of the mouth and fauces, later becoming general. There is a sense of dryness and of constriction in the throat. Persistent vomiting usually occurs, but is absent in some cases. There is diminished sensibility, with numbness, great muscular feebleness, giddiness, loss of speech, irregularity and failure of the heart's action. Death may result from shock if a large dose of the alkaloid be taken, but more usually it is by syncope.

The *treatment* should be directed to the removal of unabsorbed poison by

the stomach-pump, and washing out of the stomach with infusion of tea holding powdered charcoal in suspension. Stimulants should be freely administered.

Alkaloids from other Sources.—**Ergotine**— $C_{50}H_{52}N_2O_3$ —and **Ecbo line** are two brown, amorphous, faintly bitter, and alkaline alkaloids obtained from ergot. They are readily soluble in water and form amorphous salts. The medicinal preparations known as ergotine are not the pure alkaloid.

Colchicine— $C_{17}H_{19}NO_5$ —occurs in all portions of *Colchicum autumnale* and other members of the same genus. It is a yellowish-white, gummy, amorphous substance, having a faintly aromatic odor and a persistently bitter taste. It is slowly but completely soluble in water, forming faintly acid solutions. It forms salts which are, however, very unstable.

Concentrated HNO_3 , or, preferably, a mixture of H_2SO_4 , and $NaNO_3$, colors colchicine blue-violet. If the solution is then diluted with H_2O , it becomes yellow, and on addition of $NaOH$ solution, brick-red.

Veratrine—**Veratrina** (U. S. P.)— $C_{32}H_{52}N_2O_8$ —occurs in *Veratrum officinale*=*Asagraea officinalis*, accompanied by **Sabadilline**— $C_{20}H_{26}N_2O_5$ —**Jervine**— $C_{30}H_{46}N_2O_3$ —and other alkaloids. The substance to which the name **Veratrina**, U. S. P., applies is not the pure alkaloid, but a mixture of those occurring in the plant.

Concentrated H_2SO_4 dissolves veratrine, forming a yellow solution, turning orange in a few moments, and then, in about half an hour, bright carmine-red. Concentrated HCl forms a colorless solution with veratrine, which turns dark-red when cautiously heated.

Physostigmine—**Eserine**— $C_{15}H_{21}N_3O_2$ —is an alkaloid existing in the Calabar bean, *Physostigma venenosum*. It is a colorless, amorphous solid, odorless and tasteless, alkaline and difficultly soluble in water. It neutralizes acids completely, with formation of tasteless salts. Its salicylate—**Physostigminæ salicylas**, U. S. P.—forms short, colorless, prismatic crystals, sparingly soluble in water.

Concentrated H_2SO_4 forms a yellow solution with physostigmine or its salts, which soon turns olive-green. Concentrated HNO_3 forms with it a yellow solution. If a solution of the alkaloid in H_2SO_4 is neutralized with NH_4OH , and the mixture warmed, it is gradually colored red, reddish-yellow, green, and blue.

Emetine— $C_{28}H_{40}N_2O_5$ —an alkaloid existing in *ipecacuanha* which crystallizes in colorless needles or tabular crystals, slightly bitter and acrid; odorless, and sparingly soluble in water.

It dissolves in concentrated H_2SO_4 , forming a green solution, which gradually changes to yellow. With Fröhde's reagent it gives a red color, which soon changes to yellowish-green and then to green.

PTOMAINES, LEUCOMAINES AND TOXINES.

The name *ptomaïne*, derived from $\pi\tau\phi\mu\alpha$ ("that which has fallen," *i.e.*, a corpse), was first suggested by Selmi in 1878 to apply to a substance, or class of substances, first distinctly recognized, although not isolated, by him, which are produced by saprophytic bacteria from proteins during putrefaction. The ptomaines are sometimes referred to as "animal alkaloids," a term which is misleading, as they are produced from vegetable as well as from animal proteins, and but few of them are alkaloids in the present acceptation of the term (p. 419). The great majority, and those the best known, are monamines, diamines, guanidines, hydramines, betaïnes, or amido acids. The term "ptomaines" does not therefore apply to the members of a distinct class of chemical compounds, but to the bacterial origin of substances belonging to several distinct chemical classes and also obtainable by other methods, having in common only the two qualities that they are basic and contain nitrogen. But some ptomaines are true alkaloids. Some of the superior homologues of pyridine are putrid products. A base $C_8H_{11}N$, isomeric with collidine, formed during putrefaction of jelly-fish, on oxidation yields nicotinic acid, $C_5H_4N(COOH)$, which is also similarly produced from nicotine (p. 423), and also forms a chloroplatinate and an iodomethylate which have the characteristic properties of the like compounds produced from the pyridine bases and vegetable alkaloids. Other basic substances obtained from brown cod-liver oil, and probably formed by a modified putrefaction, are hydropyridine derivatives. Among these are a dihydrolutidine, $C_7H_{11}N$, a dihydrocollidine, $C_8H_{13}N$, and a complex hydropyridic oxyacid, called **morrhuc acid**, $HO.C_3H_5N.C_3H_6.COOH$. Indole and skatole, products of putrefaction, also come within the definition of alkaloids.

A ptomaïne may be defined as a basic compound, containing nitrogen, produced from protein material by the bacteria which cause putrefaction.

Owing to the wide variations in the chemical constitution of the ptomaines, they possess no characters by which they can be distinguished as a class. Some are strongly alkaline and basic, others only feebly so. Some are liquid, oily and volatile, others fixed and crystalline. Some are very prone to oxidation, and are active reducing agents, others are quite stable. For the same reason, no analytical method is possible by which vegetable alkaloids and ptomaines can be separated from each other *en masse*, nor are any reactions known to which all ptomaines respond while vegetable alkaloids do not, or the reverse; nor are such reactions to be expected. Certain classes of ptomaines may be identified or separated from vegetable alkaloids, but not all. Thus those which are diamines may be separated by formation of their benzoyl derivatives, but only a few ptomaines are diamines. Those ptomaines which are reducing agents give a blue color with a mixture of ferric chloride and potassium ferricyanide but all ptomaines do not reduce, and some vegetable alkaloids, such as morphine and veratrine, do. It was feared that the existence of ptomaines, whose formation begins shortly after death, and also occurs during life, might render the detection of vegetable poisons in the cadaver impossible. Such fears were by no means groundless, as there is abundant evidence that ptomaines have been mistaken for vegetable alkaloids in chemico-legal analyses. It is, however, possible to positively and certainly predicate the existence or non-existence in a cadaver of a given vegetable alkaloid, provided it has a sufficient number of characterizing reactions, but it can only be done after a thorough and conscientious examination by all physiological and chemical reactions.

Leucomaines are nitrogenous, basic substances which are produced in the bodies of animals during life as results of normal chemical processes. They are excreted in health, and if retained exert deleterious actions, more or less intense. The xanthine, or purine, bases and those of the creatine group are

leucomaines, and others occur in the urine. But, as some leucomaines, such as choline, tyrosine, and betaine, are also ptomaines, being produced by saprophytic bacteria, the line of distinction cannot be sharply drawn.

Toxines.—The name “toxine” was first used by Brieger, and by him applied to poisonous ptomaines and other toxic, basic, nitrogenous substances, obtained from the culture media of pathogenic bacteria or from animal organisms. Such are the four basic substances obtained from the culture media of the tetanus bacillus: **Tetanine**, $C_{13}H_{11}N_2O_4$, a yellow, strongly alkaline syrup; **Tetanotoxine**, $C_5H_{11}N(?)$, a volatile oil; **Spasmotoxine**, and another unnamed base of undetermined composition, all of which form deliquescent hydrochlorides, and very soluble, crystalline platinochlorides. These bases, when injected into animals, cause clonic or tonic convulsions of great intensity, terminating in death. But it has been shown that the cultures from which these basic substances are obtainable, after filtration through porcelain, are vastly more toxic than the combined bases. These therefore can only constitute a small fraction of the active material produced by the bacilli, and the more virulent, non-basic product is a toxine in the more modern sense.

In this latter sense the toxines are poisonous substances of unknown chemical composition produced by bacteria or other cells. They are not products of decomposition of the proteins, as are the ptomaines, but synthetic products, secretions, as it were, of the bacteria. They are not all members of the same chemical class. Some, the **extracellular toxines**, so called because they pass in great part into the culture media, have many resemblances to the albumoses. They are non-crystalline, soluble in water, and dialysable, are precipitated by alcohol and by ammonium sulphate, and lose their virulence when heated. The toxines of diphtheria and tetanus belong to this class. But little is known of the properties of the **intracellular toxines**, which are largely retained in the bacterial cells until these are destroyed, except that they do not dialyse, and are more resistant to heat than the extracellular toxines. The toxines of typhoid, tubercle and glanders belong to this second class.

The **toxalbumins** are substances obtained from certain seeds or secreted by animals, which are highly toxic, and have the general properties of albumoses or of globulins. They therefore differ from the toxines solely in that they are not of bacterial origin, and, furthermore, they resemble bacterial poisons more closely than vegetable alkaloids in their actions, particularly in the latent period preceding the manifestation of their effects.

Putrefaction is the decomposition of dead protein material under the influence of certain bacteria, attended by the evolution of more or less fetid products. In order that it may occur, certain **conditions** are necessary: (1) The presence of living bacteria, or of their germs; (2) the presence of moisture; (3) a temperature between 5° and 90° ; (4) an atmospheric condition suitable to the growth of the bacteria. Some of the several species of bacteria which cause putrefaction are aerobic, *i.e.*, require the presence of air for their development, while others are anaerobic, *i.e.*, they thrive best in the absence of oxygen. Proteins which have been deprived of moisture, either by drying or by the action of dehydrating agents, such as strong alcohol, do not enter into putrefaction unless water is supplied to them, when the process proceeds as usual. The temperature most favorable to putrefaction is about 40° . High or low temperatures arrest putrefaction or prevent it, the former, if sufficiently high, permanently (if the material is protected from new bacteria) by destroying the vitality of the bacteria; the latter, even if extreme, only temporarily, and so long as the low temperature is maintained.

Putrefaction may, therefore, be **prevented** either (1) by the action of agents or substances which interfere with the development of bacteria (germicides and antiseptics); (2) by the exclusion of air; (3) by the exclusion of water; (4) by a temperature below 5° or above 90° .

Putrefaction is attended by the breaking down and liquefaction of the material if it is solid; or its clouding and the formation of a scum upon the surface if it is liquid. The **products of putrefaction** vary with the conditions under which it occurs. The most prominent are: (1) inorganic products such as N, H, H_2S , NH_3 , and simple organic compounds, such as CO_2 and hydrocarbons; (2) acids of the fatty series in great abundance, and acids of the oxalic and lactic series; (3) non-aromatic monamines and diamines, such as trimethylamine, putrescine, and certain of the ptomaines; (4) aromatic products, among which are: (a) phenols, such as tyrosine, oxyaromatic acids, phenol, and cresol; (b) phenylic derivatives, such as phenyl acetic and phenyl propionic acids; (c) indole, skatole, skatole-carbonic acid, etc.; (d) ptomaines of undetermined constitution, but belonging to the aromatic series; pyridine derivatives.

Under certain imperfectly defined conditions buried protein material does not undergo ordinary putrefaction, but is converted into a substance resembling tallow, and called **adipocere**, which consists chiefly of ammonium palmitate, stearate and oleate, calcium phosphate and carbonate, and an undetermined nitrogenous substance.

Germicides are substances or agents which destroy bacteria and their germs. Mercuric chloride and heat are germicides.

Antiseptics are substances which prevent or restrain putrefaction. Antiseptics are either germicides, which prevent putrefaction by destroying the organisms which cause it, or are agents, which interfere with the development of these organisms without destroying their vitality. The salts of aluminium are antiseptic by reason of their chemical action on the proteins, although their germicidal powers are slight.

Deodorizers, or air purifiers, are substances which destroy the odorous products of putrefaction.

Disinfectants are substances which restrain infectious diseases by destroying or removing their specific poisons.

APPENDIX

TABLE OF SOLUBILITIES

FRESENIUS.

W or w = soluble in H_2O . A or a = insoluble in H_2O ; soluble in HCl, HNO_3 , or aqua regia. I or i = insoluble in H_2O and acids. W-A = sparingly soluble in H_2O , but soluble in acids. W-I = sparingly soluble in H_2O and acids. A-I = insoluble in H_2O , sparingly soluble in acids. Capitals indicate common substances.

	Aluminium.	Ammonium.	Antimony.	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper.	Ferrous.	Ferric.
Acetate.....	W	W	W	w	w	W	w	w	W	w	W
Arsenate.....	a	w	a	a	a	a	a	a	a	a	a	a
Arsenite.....	w	a	a	a	a	A	a	a
Benzoate.....	w	w	w	w	w	a	w	a
Borate.....	a	w	a	a	w-a	a	a	a	a	a	a
Bromide.....	w	W	w-a	w	w-a	w	w	w-i	w	w	w	w
Carbonate....	a	W	A	A	a	A	a	A	A	A	a
Chlorate.....	w	w	W	w	w	w	w	w	w	w	w
Chloride.....	w	W ²	W-A ⁶	W	W-A ¹⁰	W	W	W-I	W	W	W	W
Chromate.....	w	a	a	a	a	w-a	a	a	w	w
Citrate.....	w	w	a	a	w-a	w	w	w	w	W
Cyanide.....	w	w-a	a	w	a	a-i	a	a-i
Ferricyanide..	w	w	i	I	w
Ferrocyanide..	w	w-a	w	i	i	i	I
Fluoride.....	w	W	w	a-i	w	w-a	A	w	w-a	a	w-a	w
Formate.....	w	w	w	w	w	w	w	w	w	w	w
Hydrate.....	A	W	A	W	a	a	W-A	A	A	a	a	A
Iodide.....	w	W	w-a	w	a	W	w	w	w	w	W	w
Malate.....	w	w	w-a	w-a	w
Nitrate.....	w	W	W	W ¹¹	w	w	W	W	W	W	W
Oxalate.....	a	W	a	a	a	a	A	w-a	A	a	a	a
Oxide.....	A-I	...	a ⁷	W	a	a	W-A	A-I	A	A	a	A
Phosphate....	a	W ³	w-a	w-a	a	a	W-A	a	a	a	a	a
Silicate.....	A-I	a	a	a	a	a	a	a	a
Succinate....	w-a	w	w-a	w	w-a	w-a	w-a	w
Sulphate.....	W ¹	W ⁴	a	A	w	W	W-I	W-A ¹²	W ¹³	W	W	W
Sulphide.....	a	W	A ⁸	W	a	A	W-A	a-i	a	A	A	A
Tartrate.....	w	w ⁵	a ⁹	a	a	w-a	a	w	w	w	w-a	W ¹⁴

¹(Al₂)(NH₄)₂(SO₄)₄=W; (Al₂)K₂(SO₄)₄=W. ²As(NH₄)Cl₄=W; Pt(NH₄)Cl₅=W-I. ³HNa(NH₄)PO₄=W; Mg(NH₄)PO₄=A. ⁴Fe(NH₄)₂(SO₄)₂=W; Cu(NH₄)₂(SO₄)₂=W. ⁵C₄H₄O₆K(NH₄)=W. ⁶SbOCl=A. ⁷Sb₂O₃=soluble in HCl, not in HNO₃. ⁸Sb₂S₃=sol. in hot HCl, slightly in HNO₃. ⁹C₄H₄O₆K(SbO)=W. ¹⁰BiOCl=A. ¹¹(BiO)NO₃=A. ¹²(Cr₂)K₂(SO₄)₄=W. ¹³CoS=easily sol. in HNO₃, very slowly in HCl. ¹⁴(C₄H₄O₆)₄(Fe₂)K₂=W.

TABLE OF SOLUBILITIES.—Continued.

FRESenius.

W or w = soluble in H_2O . A or a = insoluble in H_2O ; soluble in HCl, HNO_3 , or aqua regia. I or i = insoluble in H_2O and acids. W-A = sparingly soluble in H_2O , but soluble in acids. W-I = sparingly soluble in H_2O and acids. A-I = insoluble in H_2O , sparingly soluble in acids. Capitals indicate common substances.

	Lead.	Magnesium.	Manganese.	Mercurous.	Mercuric.	Nickel.	Potassium.	Silver.	Sodium.	Strontium.	Stannous.	Stannic.	Zinc.
Acetate.....	W	w	w	w-a	w	w	W	w	W	w	w	w	W
Arsenate.....	a	a	a	a	a	a	W	a	W	a	a	a
Arsenite.....	a	a	a	a	a	a	w	a	w	a	a
Benzoate.....	a	w	w	a	w-a	w	w-a	w
Borate.....	a	w-a	a	a	W	a	W	a	a	a
Bromide.....	w-i	w	w	a-i	w	w	W	a	W	w	w
Carbonate.....	A	A	A	a	a	A	W	a	W	A	A
Chlorate.....	w	w	w	w	w	w	W	w	w	w	w	w
Chloride.....	W-I	W	W	A-I	W ¹⁶	W	W ²⁰	I	W	W	W	W	W
Chromate.....	A-I	w	w	a	w-a	a	W	a	w	w-a	a	w
Citrate.....	a	w	a	a	w-a	w	w	a	W	a	w-a
Cyanide.....	a	w	a	W	a-i	W	i	w	w	a
Ferricyanide.....	w-a	w	i	i	W	i	w	a
Ferrocyanide.....	a	w	a	i	W	i	w	w	a-i
Fluoride.....	a	a-i	a	w-a	w-a	w	w	w	a-i	w	w	w-a
Formate.....	w-a	w	w	w	w	w	w	w	w	w	w	w
Hydrate.....	a	A	a	a	W	W	w	a	a	a
Iodide.....	W-A	w	w	A	A	w	W	i	w	w	w	w	w
Malate.....	w-a	w	w	a	w-a	w	w-a	w	w	w	w	w
Nitrate.....	W	w	w	W	W	W	W	W	W	W	w
Oxalate.....	a	a	w-a	a	a	a	W	a	W	a	a	w	a
Oxide.....	A	A	A ¹⁵	A	A	A	W	a	W	W	a	A-I	A
Phosphate.....	a	a ³	a	a	a	a	w	a	W	a	a	a	a
Silicate.....	a	a	a	a	W	W	a	a
Succinate.....	a	w	w	a	w-a	w	w	a	w	w-a	a	w-a
Sulphate.....	A-I	W	W	w-a	W ¹⁷	W	W ¹²	W-A	W	I	w	W
Sulphide.....	A	a	a	a	A ¹⁸	A ¹⁹	W	a ²¹	W	w	a ²²	A ²²	A ²³
Tartrate.....	a	w-a	w-a	w-a	a	a	W	a	w	a	a	a

¹⁵MnO₂=sol. in HCl; insol. in HNO_3 . ¹⁶Mercurammonium chloride=A. ¹⁷Basic sulphate=A. ¹⁸HgS=insol. in HCl and in HNO_3 , sol. in aqua regia. ¹⁹See 13. ²⁰PtKCl₅=W-A. ²¹Only soluble in HNO_3 . ²²Sn sulphides=sol. in hot HCl; oxidized, not dissolved, by HNO_3 . Sublimed SnCl₄ only sol. in aq. regia. ²³Easily sol. in HNO_3 , difficultly in HCl.

Au₂S=insol. in HCl and in HNO_3 , sol. in aq. regia. AuBr₃, AuCl₃, and Au(CN)₃=w; AuI₃=a. PtS₂=insol. in HCl, slightly sol. in hot HNO_3 ; sol. in aq. regia. PtBr₄, PtCl₄, Pt(CN)₄, Pt(NO₃)₄, Pt(C₂O₄)₂, Pt(SO₄)₂=w; PtO₂=a; PtI₄=i.

INDEX



INDEX

- Absolute temperature, 13.
 zero, 13.
Absorption of gases, 11.
Acetal, 233.
Acetaldehyde, 229.
Acetaldoxime, 320.
Acetals, 232.
Acetamide, 312.
Acetanilide, 372.
Acetates, 253.
Acetol salicylate, 358.
Acetonamines, 319.
Acetone, 234.
 diethylsulphone, 287.
 dimethylsulphone, 287.
Acetonemia, 235.
Acetones, 233.
Acetonitrile, 305, 306, 313.
Acetophenone, 355.
 oxime, 355.
Acetophenyl hydrazide, 381.
Acetoxime, 320.
Acetoximes, 320.
Acetyl benzene, 355.
 benzoylaconine, 440.
 chloride, 270.
 hydroxide, 252.
 morphine, 434.
Acetylene, 329.
 series, 201, 329.
Acetylde, 329.
Achroödextrins, 246.
Acid (see also Acids).
 acetic, 252.
 acetoacetic, 266.
 acetohydroxamic, 301.
 acetylamidoacetic, 323.
 aconitic, 265.
 acrylic, 330, 331.
 allophanic, 317.
 amidoacetic, 323 (see Glycocoll).
 amidobenzoic, 356.
 amidoformic, 313, 322 (see Acid, Carbamic).
 amidoisobutylacetic, 325.
 amidovaleric, 325.
 amygdalic, 362.
Acid anhydrides, 269.
Acid, anilidoacetic, 375.
 anilindisulphonic, 371.
 anilpyroracemic, 376.
 anthranilic, 356, 374.
 antitartaric, 264.
 arachic, 256.
 arsenic, 113, 115.
 arsenous, 113.
 auric, 129.
 barbituric, 404.
 benzenedicarboxylic, 357.
 benzenemonosulphonic, 366.
 benzene sulphonic, 341.
 benzene trisulphonic, 366.
 benzhydroxamic, 376.
 benzoic, 356.
 benzoylamidoacetic, 375 (see Acid, hippuric).
 boracic, 124.
 boric, 124.
 butan, 253.
 butyric, 253.
 cacodylic, 327.
 cachoutannic, 360.
 caffaic, 360.
 caffetannic, 360.
 capric, 255.
 caprylic, 255.
 carbamic, 313.
 carbanilic, 375.
 carbazotic, 369.
 carbolic, 345 (see Phenol).
 carbonic, 261.
 chelidonic, 397.
 chloric, 79.
 chromic, 131.
 cinchomeronic, 430.
 citraconic, 265.
 citric, 265.
 comenic, 397.
 cumic, 356.
 cyanic, 307.
 cyanuric, 307, 315.
 decylic, 255.
 dextrolactic, 262.
 dextrotartaric, 264.
 diacetic, 266.
 dialuric, 404.
 dichloracetic, 253.
 dichromic, 131.
 digallic, 360.
 dihydrocyanic, 310.
 dimethylacetic, 254.
 dinitronaphtholsulphonic, 387.
 dioxibenzoic, 359.
 dioxycinnamic, 360.
 dioxymalonic, 266.
 disulphanilic, 371.
 dithiocarbamic, 316.
 elaëdic, 332.

- Acid, erythroglucic, 225.
 ethan, 252.
 ethidenelactic, 262.
 ethidenepropionic, 331.
 ethylacetic, 253.
 ethylenelactic, 263.
 ethylsulphonic, 277.
 ethylsulphuric, 268, 277.
 formic, 251.
 fulminic, 307.
 fulminuric, 308.
 fumaric, 332.
 furfurane carboxylic, 392.
 gadinic, 282.
 gallic, 359.
 glucovanillic, 362.
 glucuronic, 266.
 glutaric, 259.
 glycerophosphoric, 281.
 glycolamic, 323.
 glycollic, 262.
 glycoluric, 318.
 glycosuric, 359.
 glyoxalineamidopropionic, 396.
 glyoxylic, 265.
 graphitic, 125.
 Acid halides, aliphatic, 270.
 aromatic, 364.
 Acid, hexahydro-tetroxybenzoic, 384.
 hippuric, 375.
 homogentisinic, 359.
 homoprotocatechuic, 359.
 hydantoic, 317, 318.
 hydracrylic, 263.
 hydrazoic, 97.
 hydriodic, 82.
 hydrobromic, 80.
 hydrochloric, 76.
 hydrochloroplatinic, 148.
 hydrocyanic, 303.
 hydrofluoric, 73.
 hydrofluosilicic, 127.
 hydronitroprussic, 310.
 hydrosulphurous, 89.
 hypobromous, 81.
 hypochlorous, 79.
 hyponitrous, 100.
 hypophosphoric, 109.
 hypophosphorous, 108.
 hyposulphurous, 89, 92.
 indoleacetic, 416.
 indoleamidopropionic, 416.
 indoxyllic, 417.
 indoxylsulphuric, 417.
 iodic, 83.
 isethionic, 286.
 isobarbituric, 407.
 isobutyric, 254.
 isocyanic, 318.
 isodialuric, 407.
 isophthalic, 357.
 isopropylacetic, 254.
 isopropylbenzoic, 356.
 Acid, isostrychnic, 432.
 isothiocyanic, 308.
 isovaleric, 254.
 itaconic, 265.
 lactic, 262.
 lævolactic, 263.
 lævotartaric, 264, 265.
 lævulinic, 347.
 lauric, 255.
 laurostearic, 255.
 lithic, 406.
 maleic, 332.
 malic, 263.
 malonic, 258.
 mannosaccharic, 265.
 margaric, 255.
 meconic, 397.
 mesotartaric, 264, 265.
 mesoxalic, 266.
 metaboric, 124.
 metanitrous, 101.
 metantimonious, 122.
 metantimonous, 122.
 metaphosphoric, 109.
 metarsenic, 114.
 metarsenous, 113.
 metastannic, 146.
 metatungstic, 128.
 methan, 251.
 methylacetic, 253.
 methylethylamido propionic, 325.
 methylguanidinacetic, 302.
 monochloracetic, 253.
 morintannic, 360.
 morphinesulphuric, 434.
 morphylsulphuric, 434.
 morrhucic, 442.
 mucic, 265.
 muriatic, 76.
 myristic, 255.
 myronic, 363.
 nitric, 101.
 nitroacetic, 321.
 nitrohydrochloric, 102.
 nitrosonitric, 102.
 nitrosulphonic, 99.
 nitrous, 101.
 octylic, 255.
 oleic, 331.
 opianic, 436.
 orthoamidobenzoic, 374.
 orthoantimonious, 122.
 orthoarsenic, 113.
 orthoboric, 124.
 orthocarbonic, 109.
 orthoformic, 252.
 orthophenylsulphonic, 366.
 orthophosphoric, 108.
 osmic, 128.
 oxalic, 257.
 oxaluric, 318.
 oxanilic, 374, 375.

- Acid, oxyacetic, 262.
 oxybutyric, 263.
 oxyformic, 261.
 oxyglutaric, 263.
 oxyhydratropic, 364.
 oxymalonic, 263.
 oxyphenic, 349.
 oxypropionic, 262, 263.
 oxysuccinic, 263.
 palmitic, 255.
 paraamidobenzenesulphonic, 371.
 parabanic, 395.
 paralactic, 262.
 paratartaric, 264.
 pentathionic, 89.
 perchloric, 79.
 periodic, 83.
 persulphuric, 92.
 phenic, 345.
 phenylacetic, 356.
 phenylamidopropionic, 374.
 phenylmalonic, 356.
 phenylsulphuric, 366.
 phloretic, 364.
 phosphatic, 109.
 phosphomolybdic, 128.
 phosphoric, 108.
 phosphorous, 108.
 phosphotungstic, 128.
 phthalamic, 373.
 phthalic, 357.
 picric, 369.
 propan, 253.
 propionic, 255.
 propylacetic, 254.
 prussic, 303.
 purpuric, 404.
 pyridinedicarboxylic, 430.
 pyridinetartronic, 428.
 pyroantimonic, 122.
 pyroarsenous, 113.
 pyroboric, 124.
 pyrocatechuic, 359.
 pyrogallic, 350.
 pyromucic, 392.
 pyrophosphoric, 109.
 pyroracemic, 266.
 pyrosulphuric, 93.
 pyrotartaric, 259, 264.
 pyruvic, 264, 266.
 quercitannic, 360.
 quinic, 384, 429.
 quinotannic, 360, 429.
 quinovic, 429.
 racemic, 264, 265.
 Acid reaction, 32.
 Acid, rosolic, 350.
 saccharic, 265.
 salicylic, 358.
 salicylous, 354.
 sarcolactic, 262.
 sebasic, 332.
 silicotungstic, 128.
 Acid, sozolic, 366.
 stannic, 146.
 stearic, 255.
 strychnic, 432.
 succinic, 259.
 sulphanilic, 371.
 sulphydric, 85.
 sulphocarbamic, 316.
 sulphocyanic, 308.
 sulphovinic, 268, 277.
 sulphuric, 90.
 sulphurous, 89.
 tannic, 360.
 tartaric, 239, 264, 265.
 tartronic, 263.
 terebic, 384.
 terephthalic, 357.
 terpenylic, 384.
 tetraboric, 124.
 tetrathionic, 89.
 thioacetic, 287.
 thiobenzoic, 365.
 thiocarbamic, 316.
 thiocyanic, 308.
 thiosulphuric, 92.
 trichloroacetic, 253.
 trichromic, 131.
 tricyanic, 307.
 trihydrocyanic, 310.
 trinitrophenic, 369.
 trithionic, 89.
 uric, 406.
 uroleucic, 359.
 urous, 410.
 valerianic, 254.
 valeric, 254.
 vanillic, 354.
 xanthic, 410.
 Acids, 36, 39 (see Acid).
 acetic series, 250.
 alcohol, 259.
 aldehyde, 265.
 alkyl benzoic, 356.
 amic, 310, 313.
 amido, 321.
 butyric, 325.
 caproic, 325.
 cinnamic, 374.
 phenyl, 373, 374.
 propionic, 325.
 valeric, 325.
 anil, 376.
 anilic, 375.
 anilido, 374, 375.
 aromatic amido, 373.
 carboxylic, 355.
 dioxycarboxylic, 358.
 monocarboxylic, 355.
 polycarboxylic, 356.
 trioxycarboxylic, 359.
 atomicity of, 259.
 basicity of, 36, 259.

- Acids, benzene dicarboxylic, 357.
 disulphonic, 366.
 benzoic series, 355.
 camphoric, 384.
 caproic, 254.
 carbopyridic, 397.
 carboxylic, 250.
 cresylic, 347.
 dibasic, 36.
 dicarboxylic, 265.
 dioxydicarboxylic, 264.
 dioxyethylene succinic, 264.
 dioxymonocarboxylic, 358.
 dioxyphenyl, 359.
 dioxytoluic, 359.
 fatty, 250.
 hexan, 254.
 hexylic, 254.
 hydroaromatic, 383, 384.
 hydrophthalic, 357.
 hydroxamic, 300, 301, 376.
 indolecarboxylic, 415.
 ketonic, 266.
 lactic, 262.
 mannosaccharic, 265.
 mineral, 77.
 monamido, 321.
 monobasic, 36.
 monocarboxylic aromatic, 355.
 monoketone monocarboxylic, 266.
 monoxydicarboxylic, 263.
 monoxymonocarboxylic, 357.
 naphthol sulphonic, 387.
 nitro, 321, 370.
 nitrobenzenic, 370.
 nitrobenzoic, 370.
 of antimony, 122.
 arsenic, 113.
 nitrogen, 100.
 phosphorus, 107.
 sulphur, 89.
 olefinedicarboxylic, 332.
 oleic, 331.
 ortho, 108.
 oxalic series, 256.
 oxyacetic, 260.
 oxyaldehyde, 266.
 oxybenzoic, 357.
 oxybutyric, 263.
 oxyketone, 266.
 oxypropionic, 262.
 oxytricarboxylic, 265.
 paraffin dicarboxylic, 256.
 monocarboxylic, 250.
 pentan, 254.
 phenol carboxylic, 357.
 phenyl amido, 373, 374.
 fatty, 356.
 propionic, 356.
 phthalic, 356.
 polybasic, 36.
 pyrrolidincarboxylic, 393.
 radical of, 46.
- Acids, residue of, 46.
 saccharic, 265.
 sulphinic, 277, 286, 366.
 sulphonic, 277, 284, 286, 365.
 sulphurous, 89.
 tannic, 360.
 tartaric, 239, 264.
 tetroxydicarboxylic, 265.
 thiocarbamic, 316.
 thiosulphonic, 286.
 toluenesulphonic, 366.
 tribasic, 36.
 trioxymonocarboxylic, 359.
 valerianic, 254.
 valeric, 254.
 volatile fatty, 250.
- Acidulous elements, 52, 73.
- Acidyl halides, 270.
 hydroxides, 250.
- Acidylences, 256.
- Aconine, 440.
- Aconite alkaloids, 440.
- Aconitine, 440.
- Acroleine, 330.
- Acrose, 240.
- Acyclic compounds, 199, 201.
- Acylation, 284.
- Addition, 197.
- Adenine, 412.
- Adipocere, 444.
- Adjacent positions, 338.
- Adonite, 225.
- Æsculetin, 362.
- Æsculin, 362.
- Affinity, 48.
- After-damp, 204.
- Air, *See* Atmospheric air.
- Alabaster, 169.
- Alanine, 375.
- Alanines, 322, 325, 375.
- Albite, 180.
- Alcohol, 214, 217 (*see* Alcohols).
 absolute, 215, 217.
 acids, 259.
 allyl, 330.
 amidoethyl, 319.
 amylic, 220.
 benzylic, 352.
 butylic, 220.
 dehydratum, 217.
 denatured, 218.
 dilutum, 217.
 esters, 275.
 ethylene, 222.
 ethylic, 214.
 isobutylic, 220.
 methylic, 214.
 nitroethylic, 319.
 oxybenzylic, 352.
 propenyl, 223.
 tropan, 425.
 vinyl, 214.
 wood, 214.

- Alcoholates, 213.
 Alcoholic beverages, 218.
 fermentation 215, 218.
 Alcohols, 210.
 amido, 319.
 amylic, 220.
 aromatic, 351.
 butyl, 220.
 camphan, 383.
 cinnamic, 352.
 diatomic, 221, 352.
 dihydric, 221, 352.
 diphenyl, 389.
 heptatomic, 225.
 hexatomic, 225.
 hexahydric, 225.
 hydroaromatic, 382.
 iso, 211.
 menthan, 383.
 monoatomic, 211.
 monohydric, 211.
 nomenclature of, 211, 221.
 nonatomic, 225.
 octatomic, 225.
 oxyphenyl, 352.
 pentatomic, 225.
 pentahydric, 225.
 polyatomic, 224.
 polyhydric, 224.
 primary, 211, 212, 213.
 propyl, 219.
 ring, 382.
 secondary, 211, 212, 214, 352.
 tertiary, 211, 212, 214, 352.
 tetraatomic, 225.
 tetrahydric, 225.
 triatomic, 223, 352.
 trihydric, 223, 352.
 Aldehyde, acetic, 229.
 acids, 265.
 acrylic, 330.
 ammonia, 227, 230, 296, 319.
 anisic, 354.
 benzoic, 353.
 formic, 228.
 glyceric, 237.
 glycolyl, 237.
 hydrazones, 321.
 methylprotocatechuic, 354.
 salicylic, 354.
 Aldehydes, 225, 226.
 aromatic, 353.
 olefine, 330.
 Aldehydrazones, 380.
 Aldoses, 236.
 Aldoximes, 320.
 Ale, 218.
 Algaroth, powder of, 121.
 Aliphatic compounds, 199, 201.
 unsaturated, 327.
 Alizarin, 388.
 Alkali, 149.
 carbonated, 149.
 caustic, 149.
 metals, 149.
 volatile, 95, 149.
 Alkaline earths, metals of, 168.
 reaction, 33.
 Alkaloids, 419.
 aconite, 440.
 cinchona, 428.
 classification of, 421.
 general reactions of, 421.
 isoquinoline, 421, 433.
 loganiaceæ, 431.
 nomenclature of, 420.
 opium, 434, 437.
 phenanthrene, 422, 433.
 piperideine, 421.
 piperidine, 421, 422.
 properties of, 420.
 pyridine, 421.
 pyrrolidine, 421.
 piperidine, 421, 424.
 pyridine, 421, 423.
 quinoline, 421, 429.
 strychnos, 431.
 tropan, 421, 424.
 Alkanes, 202.
 Alkaptonuria, 359.
 Alkarsin, 326.
 Alkyl, 202.
 halides, 205.
 hydroxides, 211.
 pyridines, 398.
 pyridinium iodides, 397.
 ureas, 316.
 Alkylation, 284.
 Alkylenes, 221.
 Allantoin, 395.
 Allene, 330.
 Allometa position, 339.
 Allortho position, 339.
 Allotropy, 9.
 Alloxan, 405.
 Alloxantin, 404.
 Alloxuric bases, 409.
 Alloys, 185.
 Allyl alcohol, 330.
 amine, 333.
 isothiocyanate, 333.
 oxide, 333.
 sulphide, 333.
 Allylene, 330.
 Alphenols, 352.
 Alumina, 178.
 Aluminates, 178.
 Aluminium, 178.
 bronze, 178.
 chloride, 179.
 group, 177.
 hydroxide, 178.
 oxide, 178.
 silicates, 180.
 sulphates, 179.
 Alums, 179.

- Amalgams, 185.
Amanitine, 296.
Amide nitrogen, 293.
Amidines, 300.
Amido acetaldehyde, 319.
 acetones, 319.
 acids, 321.
 aromatic, 367.
 alcohols, 319.
 aldehydes, 319.
 azo compounds, 379.
 benzenes, 371.
 benzol, 371.
 group, 293.
 ketodihydropyrimidine, 403.
 ketones, 319.
 ketopurine, 411.
 paraffins, 292.
 phenyl acids, 367.
 phenylalanine, 375.
 phenols, 373.
 purine, 412.
 xylenes, 372.
Amidoximes, 300, 376.
Amides, 310 (see Monamides, Diamides).
 aromatic, 367, 373.
 mixed, 310.
 of dicarboxylic acids, 313.
Amine bases, 292.
 nitrogen, 293.
Amines, 292 (see Monamines, Diamines).
 aromatic, 367.
Amino group, 293.
Ammelide, 315.
Ammonia, 95.
 aldehyde, 227, 230, 296, 319.
 bismuth of, 167.
 caustic, 166.
Ammonias, compound, 293.
Ammonio-magnesium phosphate, 174.
Ammonium, 96, 165.
 acetate, 167.
 alum, 179.
 amalgam, 166.
 bromide, 167.
 carbonates, 167.
 chloride, 96, 166.
 compounds, 165.
 cyanate, 307.
 derivatives, 292.
 hydroxide, 96, 106.
 iodide, 167.
 nitrate, 167.
 sesquicarbonate, 167.
 sulphates, 167.
 sulphydrate, 166.
 sulphides, 166.
 theory, 165.
Amorphous substances, 4.
Ampère, 21.
Amphoteric elements, 53, 129.
Amphoteric reaction, 33.
Amygdalin, 303, 362.
Amyl nitrate, 279.
 nitrite, 279.
Amylene, 330.
 hydrate, 221.
Amylum, 245.
Analysis, 33, 63.
 organic, 194.
Analytical characters of alcohol, 218.
 aluminium, 180.
 ammonia, 96.
 ammonium, 167.
 aniline, 371.
 antimony, 123.
 arsenic, 116.
 atropine, 426.
 barium, 172.
 bismuth, 144.
 bromidion, 81.
 brucine, 433.
 cadmium, 177.
 calcium, 171.
 carbolic acid, 346.
 carbon dioxide, 274.
 chloridion, 78.
 chloroform, 206.
 chromium, 131.
 cobalt, 181.
 cocaine, 428.
 coniine, 422.
 copper, 183.
 cyanides, 304.
 fluorine, 74.
 formaldehyde, 229.
 glycerol, 224.
 gold, 130.
 hydrogen, 59.
 dioxide, 70.
 sulphide, 87.
 iodidion, 83.
 iron, 137.
 lead, 141.
 lithium, 150.
 magnesium, 175.
 manganese, 132.
 mercury, 189.
 morphine, 435.
 nickel, 181.
 nicotine, 424.
 nitrates, 102.
 nitrobenzene, 368.
 oxalates, 258.
 oxygen, 61.
 ozone, 62.
 phenol, 346.
 phosphates, 109.
 phosphorus, 106.
 potassium, 163.
 quinine, 429.
 silver, 165.
 sodium, 156.
 strontium, 171.

- Analytical characters of strychnine, 432.
 sulphates, 92.
 sulphides, 87.
 sulphites, 89.
 sulphur dioxide, 88.
 tin, 146.
 zinc, 177.
 Anethol, 354.
 Anglesite, 138.
 Anhydride, acetie, 269.
 antimonic, 122.
 antimonous, 121.
 arsenic, 113.
 arsenous, 112.
 benzoic, 364.
 boric, 124.
 carbonic, 272.
 chromic, 130.
 hypochlorous, 79.
 molybdic, 128.
 nitric, 100.
 nitrous, 99.
 phosphoric, 107.
 phosphorous, 107.
 phthalic, 364.
 plumbic, 139.
 salicylic, 364.
 silicic, 127.
 succinic, 259.
 sulphuric, 88.
 sulphurous, 87.
 titanic, 145.
 tungstic, 128.
 Anhydrides, 46, 61.
 acid, 269.
 aromatic, 364.
 halide, 270.
 thio, 87.
 Anhydroeegonine, 427.
 Anilido acids, 374, 375.
 Anilides, 372.
 Aniline, 371.
 dyes, 373, 376.
 Anions, 20, 35, 45.
 Anisidines, 369, 372.
 Anisol, 360.
 Annidalin, 348.
 Anode, 19.
 Anthracene, 386.
 oil, 341.
 Anthracite, 125.
 Antifebrine, 372.
 Antimony, 120.
 acids of, 122.
 black, 122.
 butter of, 121.
 chlorides of, 121.
 erosus of, 122.
 crude, 122.
 glass of, 122.
 liver of, 122.
 organic compounds of, 326.
 oxides of, 121.
 Antimony, pentachloride, 121.
 pentasulphide, 122.
 pentoxide, 122.
 sulphides of, 122.
 tartrated, 162.
 trichloride, 121.
 trioxide, 121.
 trisulphide, 122.
 Antimonyl potassium tartrate, 162.
 Antipyrine, 394.
 salicylate, 394.
 Antiseptics, 444.
 Apoeatropine, 427.
 Apomorphine, 434, 436.
 Apoquinine, 430.
 Aqua ammoniac, 96.
 destillata, 67.
 fortis, 101.
 regia, 77, 102.
 sapphirina, 183.
 Arabin, 246.
 Arabinose, 237.
 Arecaïne, 422.
 Argol, 161.
 Argon, 72.
 Arieine, 429.
 Aristol, 348.
 Aromatic compounds, 200, 334, 336.
 Arragonite, 170.
 Arsenates, 115.
 Arsenic, 110, 112, 115.
 antidote, 115.
 bisulphide, 114.
 halides, 112.
 organic compounds of, 326.
 pentasulphide, 114.
 pentoxide, 113.
 trichloride, 112.
 triiodide, 112.
 trioxide, 112, 115.
 trisulphide, 114.
 Arsenical greens, 115.
 Arsenites, 113.
 Arsine, 111.
 dimethyl, 326.
 Arsines, 326.
 Artesian wells, 65.
 Artifacts, 30.
 Asbestos, 173.
 Aselline, 282.
 Aseptol, 366.
 Asymmetric carbon atom, 329.
 Atmospheres, 4.
 Atmospheric air, 72, 94.
 ammoniacal compounds in, 95.
 analysis of, 274.
 carbon dioxide in, 95, 272, 274.
 nitrous acid in, 95.
 rare elements in, 72.
 solid particles in, 95.
 sulphurous acid in, 95.
 water in, 95.
 Atom, 25, 26.

- Atomic rearrangement, 33.
 - theory, 24.
 - weight, 26.
- Atomicity, 30, 37.
- Atropamine, 427.
- Atropine, 425.
- Auric chloride, 129.
- Aurin, 350.
- Auroamidoimide, 308.
- Aurous chloride, 129.
- Avogadro, postulate of, 24.
- Azines, 398.
- Azobenzene, 378, 379.
- Azo compounds, 367, 376, 378.
 - dyes, 376.
- Azoimide, 97.
- Azoles, 393.
- Azonaphthol compounds, 387.
- Azo nitrogen, 293.
- Azote, 94.
- Azoxybenzene, 378.
- Azoxy compounds, 378.

- Baking powders, 161.
- Balsams, 385.
- Barium, 171.
 - carbonate, 172.
 - chloride, 172.
 - dioxide, 172.
 - hydroxide, 172.
 - monoxide, 171.
 - nitrate, 172.
 - oxides, 171.
 - sulphate, 172.
- Baryta water, 171, 172.
- Bases, 36, 39.
 - acidity of, 37.
 - atomicity of, 37.
- Bassorin, 246.
- Basyous elements, 53, 149.
- Battery, galvanic, 19.
- Bauxite, 178.
- Beer, 218.
- Belladonnine, 427.
- Benzamide, 356, 373.
- Benzene, 334, 341.
 - amido, 371.
 - amido derivatives of, 367, 371.
 - azomethane, 378.
 - azoxy, 378.
 - halides, 343.
 - homologues of, 341.
 - hydroxylamine derivatives of, 367, 370.
 - imido derivatives of, 367.
 - nitro, 367.
 - nitro derivatives of, 367.
 - nitrogen derivatives of, 367.
 - nitroso derivatives of, 367.
 - nucleus, 334.
 - oxygen compounds of, 343.
 - ring, 334.
 - sulphochloride, 366.
- Benzenyl, 356.
 - amidine, 356.
 - amidoxime, 376.
- Benzhydrol, 389.
- Benzidine, 379.
- Benzine, 204.
- Benzol, 341.
- Benzolene, 204.
- Benzonitrile, 373.
- Benzophenol, 345.
- Benzopyridine, 414.
 - bases, 418.
- Benzopyrrole, 415.
- Benzoquinone, 351.
- Benzosol, 349.
- Benzosulphinide, 366.
- Benzoyl, 343.
 - amide, 373.
 - chloride, 364.
 - ecgonine, 427.
 - glycocoll, 375.
 - hydride, 353.
 - morphine, 434.
 - sulphonic imide, 366.
- Benzyl, 343.
 - benzene, 388.
 - chloride, 343.
 - hydrate, 352.
- Betaine, 298.
 - trimethylacetic, 298.
- Betaïnes, 297.
- Beverages, alcoholic, 218.
- Bieberich scarlet, 387.
- Bilineurin, 296.
- Bismark brown, 101.
- Bismuth, 142.
 - hydroxide, 143.
 - magma of, 143.
 - milk of, 143.
 - nitrate, 143.
 - of ammonia, 167.
 - oxides of, 143.
 - subcarbonate, 143.
 - subnitrate, 143.
 - trichloride, 143.
 - trinitrate, 143.
 - trioxide, 143.
- Bismuthates, 142.
- Bismuthyl, 142.
 - carbonate, 143.
 - chloride, 143.
 - hydroxide, 143.
 - nitrate, 143.
- Biuret, 315, 317.
- Black wash, 185.
- Bleaching powder, 169.
- Blende, 175.
- Blue stone, 183.
- Boiling, 15, 16.
 - point, 12, 16.
 - absolute, 16.
- Bone ash, 170.
 - black, 126.

- Bone oil, 397.
 phosphate, 170.
Borax, 154, 214.
Bordeaux dyes, 387.
Borneo camphor, 383.
Borneol, 383.
Boroglyceride, 124.
Boron, 123.
 trioxide, 124.
Braunite, 131.
Brimstone, 84.
British gum, 246.
Bromamide, 312.
Bromidion, 81.
Bromides, 80.
Bromine, 80.
Bromoform, 207.
Bromophenols, 348.
Brucine, 433.
Butalanine, 325.
Butyl morphine, 434.
Butyrolactam, 393.
- Cacodyl, 326.
 cyanide, 327.
 oxide, 326.
Cadaverine, 299.
Cadet, liquid of, 326.
Cadmium, 177.
Cæsium, 163.
Caffeine, 411.
Calamine, 176.
Calcium, 168.
 acetylide, 329.
 carbide, 169.
 carbonate, 170.
 chloride, 169.
 group, 168.
 hydrate, 169.
 hydroxide, 169.
 hypoehlorite, 169.
 oxalate, 170.
 oxide, 168.
 phosphates, 170.
 plumbite, 139.
 sulphate, 169.
Calcespar, 170.
Calomel, 186.
Calorie, 12.
Camphan alcohols, 383.
Camphol, 383.
Camphor, 384.
 Borneo, 383.
 Japan, 384.
 laurel, 384.
 monobromo, 384.
Camphors, 384.
Camphoryl morphine, 434.
Campobello, yellow, 387.
Cane sugar, 242.
Caramel, 243.
Carbamide, 314.
Carbamines, 306.
- Carbides, 329.
Carbimide, 318.
Carbinol, 211, 214.
 butyl, 220.
 diethyl, 221.
 diphenyl, 389.
 diphenyltoluyl, 389.
 ethyl, 219.
 ethyldimethyl, 221.
 ethylmethyl, 220.
 isobutyl, 220.
 isopropyl, 220.
 methyl, 214.
 methyloisopropyl, 221.
 methylpropyl, 221.
 phenyldimethyl, 352.
 phenylmethyl, 352.
 propyl, 220.
 trimethyl, 220.
 triphenyl, 389.
Carbocyclic compounds, 200, 334, 335.
Carbodiimides, 372.
Carbohydrates, 235.
 tests for, 247.
Carbolates, 346.
Carbolic oil, 341.
Carbo animalis, 126.
 ligni, 125.
Carbon, 124.
 amorphous, 125.
 compounds of, 191.
 dichloride, 207.
 dioxide, 272.
 disulphide, 287.
 group 124.
 metallic, 125.
 monoxide, 270.
 hemoglobin, 271, 273.
 oxides of, 270.
 oxysulphide, 288.
 tetrabromide, 207.
 tetrachloride, 207.
 trichloride, 207, 280.
 valence of, 196.
Carbonic acid gas, 272.
Carbonic anhydride, 272.
 oxide, 270.
Carbonous oxide, 270.
Carbonyl, 198.
 chloride, 271.
 diurea, 318.
Carborundum, 127.
Carbotriamine, 301.
Carboxime, 320.
Carboxyl, 198.
Carbylamines, 295, 306.
Carbyloxime, 307.
Carnallite, 157.
Carnine, 409, 413.
Carvaerol, 348.
Carvol, 348.
Cassel yellow, 140.
Cassiterite, 145, 146.

- Cassius' purple, 129.
 Catalysers, 58.
 Cathode, 19.
 Cations, 20, 35, 45.
 Celestine, 171.
 Cellulin, 247.
 Celluloid, 247.
 Cellulose, 247.
 nitro, 247.
 Celsius' scale, 12.
 Centigrade scale, 12.
 Cerebrin, 241.
 Cerebrose, 241.
 Ceruse, 141.
 Cerusite, 141.
 Cetaceum, 279.
 Cetin, 279.
 Cetyl palmitate, 279.
 Chains, 199, 200.
 Chalk, 170.
 precipitated, 170.
 prepared, 170.
 Characterizing groups, 198.
 Charcoal, 125.
 animal, 126.
 wood, 125.
 Chelidonine, 397.
 Chemical affinity, 48.
 change, 1.
 displacement, 48.
 energy, 48.
 equilibrium, 49.
 equivalent, 31.
 force, 48.
 stability, 48.
 system, 49.
 Chemism, 48.
 Chemistry, 1.
 general, 1.
 inorganic, 57.
 organic, 191, 192.
 Chinovose, 237.
 Chloral, 230, 231.
 alcoholate, 232.
 hydrate, 231.
 Chloralamide, 312.
 Chloraldide, 232.
 Chloralide, 232.
 Chloralimide, 312.
 Chloralum, 179.
 Chloride of lime, 169.
 Chloridion, 78.
 Chlorides, 78.
 Chlorinated lime, 169.
 Chlorine, 74.
 group, 73.
 monoxide, 79.
 peroxide, 79.
 tetroxide, 79.
 water, 75.
 Chlorobenzenes, 343.
 Chloroform, 206.
 Chlorophenols, 348.
 Chlorophyll, 228, 274.
 Chloroplatinates, 148.
 Chlorozone, 155.
 Choline, 296.
 Chromates, 131.
 Chrome yellow, 140.
 Chromium, 130.
 oxides of, 130.
 sulphates of, 131.
 Cider, 219.
 Cinchona alkaloids, 428, 430.
 red, 429.
 Cinchonicine, 430.
 Cinchonidine, 430.
 Cinchonine, 429, 430.
 Cineol, 383.
 Cinnabar, 184.
 Circuit, electric, 19.
 Cisterpin, 383.
 Classification of alkaloids, 421.
 of aromatic compounds, 339.
 of carbocyclic compounds, 335, 339.
 of carbohydrates, 236.
 of elements, 51.
 of heterocyclic compounds, 390.
 of organic compounds, 199.
 Clay, 180.
 Closed chain compounds, 200, 334.
 Coal, 125.
 tar, 341.
 Cobalt, 181.
 Cocaine, 427.
 Codeine, 436, 438.
 Cohesion, 4.
 Coke, 126.
 Colchicine, 441.
 Collidines, 398.
 Colloids, 9.
 Colophony, 382.
 Columbium, 128.
 Combinations, 33.
 Combustion, 60.
 supporters of, 60.
 Composition, 46, 196.
 Compound ammonias, 293.
 Compounds, 22.
 Compounds, acyclic, 201.
 aliphatic, 201.
 aromatic, 200, 334, 336.
 carbocyclic, 200, 334, 335.
 closed chain, 200, 334.
 cyclic, 200, 334.
 fatty, 201.
 heterocyclic, 334, 389, 414.
 hexacarbo-cyclic, 336.
 monobenzenic, 341.
 open chain, 201.
 organic, 192, 201.
 saturated, 196, 201.
 unsaturated, 197.
 Concentration, 9, 37.
 Condensation, 11, 16, 229.
 Condensed carbocyclic compounds, 385

- Condensed heterocyclic compounds, 414.
 nuclei, 385.
Condensing agents, 229.
Conductors, 17.
Condy's fluid, 155.
Congelation, 15.
Conhydrine, 422.
Coniferin, 354, 362.
Coniceïne, 422.
Coniïne, 398, 422.
Consecutive positions, 338.
Constitution, 46, 193, 196.
Contact agent, 268.
Copper, 181.
 acetates, 183.
 acetylides, 329.
 ammonio-sulphate, 183.
 chlorides, 182.
 group, 181.
 hydroxides, 182.
 oxides, 182.
 reduction tests, 248.
Copperas, 135.
Coprolites, 170.
Corallin, 350.
Cordials, 219.
Corrosive sublimate, 187.
Corrosives, 78, and see Toxicology.
Corundum, 178.
Cosmoline, 204.
Cotarnine, 436, 438.
Coulomb, 21.
Cream of tartar, 161.
Creasol, 347.
Creosote, 347.
 oil, 341.
Creatine, 302.
Creatinine, 302.
Creolin, 347.
Cresols, 347.
Cresylols, 347.
Crith, 58.
Cryolyte, 73, 178.
Crystallization, 4.
 water of, 8, 63, 64.
Crystalloids, 9.
Crystals, 5.
Cupric acetate, 183.
 arsenite, 183.
 chloride, 182.
 hydroxide, 182.
 nitrate, 182.
 oxide, 182.
 sulphate, 183.
Cuprous chloride, 182.
 hydroxide, 182.
 oxide, 182.
Curarine, 433.
Cyamelide, 307.
Cyanamide, 309.
Cyanidine, 414.
Cyanides, 303, 305.
Cyanobenzene, 373.
Cyanogen, 303.
 chlorides, 304.
 compounds, 303.
 hydride, 303.
 sulphydrate, 308.
Cyclic compounds, 200, 334.
Cyclodiolefine, 335.
Cyclohexane, 335.
Cycloparaffins, 335.
Cyclotriolefine, 335.
Cymene, 342.
Cymogene, 204.
Cytosine, 403.
Daphnetin, 362.
Daphnin, 362.
Deamidation, 323.
Decompositions, 33.
 double, 33, 37.
 primary, 34.
Defuselation, 220.
Dehydromorphine, 434.
Deliquescence, 15, 16.
Density absolute, 3.
 relative, 3.
Deodorizers, 444.
Deoxidation, 58.
Deoxystrychnine, 432.
Derived substances, 208.
Dextrin, 246.
Dextrose, 240.
Diabetic sugar, 240.
Diacetine, 223.
Diacetonamine, 319.
Diacetylene series, 201.
Diacetylenediamine, 298.
Diacetylmorphine, 434.
Diachylon, 139.
Dialdehydes, 233.
Dialysis, 9.
Diamide, 96.
Diamides, 310.
 primary, 314.
Diamidodiphenol, 379.
Diamine diacetylene, 299.
 diethylene, 400.
 ethylene, 299.
 pentamethylene, 299.
 phenylene, 380.
 tetramethylene, 299.
 trimethylene, 299.
Diamines, 292, 296, 298.
Diamond, 125.
Diastase, 214.
Diazines, 399.
Diazo,
 amido compounds, 367.
 benzene chloride, 376.
 compounds, 376.
 dyes, 379.
 nitrogen, 293.
Diazoles, 393, 394.
Diazotizing, 377.

- Dibromomethyl bromide, 207.
 Dicacodyl, 326.
 Dichlormethane, 206.
 Dichlormethyl chloride, 206.
 Dicyanogen, 307.
 Diethylcarbinol, 221.
 Diethylenediamine, 400.
 Diethylmalonylurea, 404.
 Diethyl sulphite, 277.
 Diffusion of liquids, 9.
 Diglycerides, 223, 280.
 Digitaliresin, 363.
 Digitalis glucosides, 363.
 Digitalin, 363.
 Digitalose, 363.
 Digitogenin, 363.
 Digitonein, 363.
 Digitonin, 363.
 Digitoxin, 363.
 Dihydrobenzenes, 335.
 Dihydrofurfurane, 392.
 Dihydropyridines, 398.
 Dihydropyrrole, 393.
 Dihydrostrychnoline, 432.
 Diimines, 296.
 Diindoxyl, 418.
 Diiodomethyl iodide, 207.
 Diketones, 233, 235, 354.
 Diketopurine, 410.
 Diketotetrahydroglyoxalin, 395.
 Diketotetrahydropyrimidine, 401.
 Dimethyl amine, 295.
 arsine, 326.
 benzenes, 342.
 indoles, 415.
 ketone, 234.
 malonylurea, 404.
 pyrazolon, 395.
 pyridines, 398.
 Dimorphism, 8.
 Dinitrobenzenes, 368.
 Dinitronaphthols, 387.
 Dinitrophenols, 369.
 Dinitrosoresorcinol, 370.
 Diolefines, 201, 330.
 Diols, 221.
 Dionine, 434.
 Dioses, 236, 237.
 Dioxindole, 374.
 Dioxycetone, 237.
 Dioxyanthraquinone, 388.
 Dioxymethylanthraquinone, 388.
 Dioxypurine, 410.
 Diphenyl, 388.
 acetylene, 388.
 benzene, 388.
 Diphenylene diketone, 387.
 Diphenyl ethylene, 389.
 hydrazine, 379.
 methane, 388.
 olefines, 388.
 oxide, 360.
 paraffins, 338.
 Disaccharides, 236, 241.
 Disacryl, 331.
 Disdiazooamido compounds, 377, 378.
 Disinfectants, 444.
 Displacement, 48.
 Dissociation, 35, 64.
 Distillation, 16, 67.
 fractional, 16.
 Diureides, 317.
 Divisibility, 2.
 Dolomite, 174.
 Dulcin, 225.
 Dulcitan, 225.
 Dulcite, 225.
 Dulcitol, 225.
 Dulcose, 225.
 Dutch liquid, 280, 328.
 Dyads, 30, 31.
 Ebullition, 15.
 Ecboline, 441.
 Ecgonine, 398, 427.
 Efflorescence, 9.
 Elayl, 327.
 chloride, 280.
 Electric circuit, 19.
 conductance, 20.
 conductivity, 20.
 current, 19.
 resistance, 20.
 units, 21.
 Electricity, 17.
 galvanic, 18.
 negative, 17.
 positive, 17.
 resinous, 17.
 vitreous, 17.
 Electrodes, 19.
 Electrochemical series, 33, 34.
 Electrolysis, 20, 33.
 Electrolyte, 20.
 Electromotive force, 20.
 Electronegative, 33, 34.
 Electropositive, 33, 34.
 Elements, 21, 27.
 acidulous, 52, 73.
 amphoteric, 53, 129.
 basylous, 53, 149.
 classification of, 51.
 electronegative, 33, 34, 52.
 electropositive, 33, 34, 53.
 equivalence of, 30.
 in earth's crust, 21.
 in human body, 21, 22.
 typical, 52, 57.
 which form no compounds, 52, 72.
 Elutriation, 170.
 Emerald, 178.
 Emery, 178.
 Emetine, 441.
 Emulsifying agents, 282.
 Emulsin, 361.
 Emulsion, 282.

- Energy, 3.
 chemical, 48.
 kinetic, 3.
 potential, 3.
- Enzymes, 216.
- Eosin, 350.
- Epiguanine, 413.
- Episarkine, 409, 413.
- Epsom salt, 173.
- Equations, 32.
- Equilibrium, apparent, 50.
 chemical, 49.
 dynamic, 49.
 heterogeneous, 49.
 homogeneous, 49.
 real, 49.
- Equivalence, 30.
- Equivalent, 37.
 chemical, 31.
 osmotic, 9.
- Ergotine, 441.
- Erythrin, 224.
- Erythrite, 224.
- Erythrodextrin, 246.
- Erythrol, 224.
- Erythrose, 237.
- Eserine, 441.
- Essence of Mirbane, 367.
 of turpentine, 382.
- Essences, 282.
- Ester, acetoacetic, 278.
 malonic, 279.
 methylenemalonic, 332.
 sulphates, 367.
- Esters, 267, 275.
 alcohol, 275.
 dioxymalonic, 266.
 haloid, 205, 279.
 hyposulphurous, 277.
 isothiocyanic, 308.
 of carbamic acid, 313.
 of dihydric alcohols, 279.
 of glycerol, 280.
 of glycols, 279.
 of monohydric alcohols, 276.
 of oxyacids, 283.
 of trihydric alcohols, 280.
 orthoformic, 277.
 oxymalonic, 266.
 thiophosphoric, 285.
 sulphurous, 277.
- Ethanal, 229.
- Ethene, 327.
 chlorhydrine, 222.
 compounds, 328.
 glycol, 222.
 homologues of, 328.
 series, 327.
- Ethenylamidoxime, 300.
- Ether, acetic, 278.
 allylic, 333.
 dimethylpyrocatechuic, 349.
 ethylic, 268.
- Ether, ethylphenyl, 361.
 hydriodic, 208.
 hydrobromic, 208.
 hydrochloric, 208.
 methylphenyl, 360.
 monomethylpyrocatechuic, 349.
 muriatic, 208.
 nitric, 276.
 nitrous, 276.
 ozonic, 70.
 petroleum, 204.
 phenyl, 360.
 propargylethyl, 333.
 sulphuric, 268, 277.
- Ethers, 267.
 compound, 267, 275.
 haloid, 205.
 mixed, 267.
 phenyl, 360.
 simple, 209, 267.
- Ethidene chloride, 328.
 compounds, 328.
 hydroxamine, 319.
 hydroxylamine, 296.
- Ethine, 329.
- Ethol, 279.
- Ethyl acetate, 278.
 acetoacetate, 278.
 benzene, 342.
 borate, 124.
 bromide, 208.
 carbinol, 219.
 chloride, 208.
 dimethylcarbinol, 221.
 hydroxide, 214.
 iodide, 208.
 malonate, 279.
 mercaptan, 285.
 methylcarbinol, 220.
 morphine, 434.
 nitrate, 276.
 nitrite, 276.
 oxide, 268.
 pyridines, 398.
 strychnium iodide, 432.
 sulphate, 277.
 sulphydrate, 285.
 urethane, 313.
- Ethylene, 327.
 alcohol, 222.
 chlorhydrine, 279.
 chloride, 280, 328.
 compounds, 328.
 diamine, 299.
 ethenyl amidene, 299.
 glycol, 222.
 hydroxide, 222.
 oxide, 269.
- Ethylidene compounds, 328.
- Eucalyptol, 383.
- Eucalyptol, 383.
- Euphorine, 314.

- Evaporation, 15.
 Exalgine, 372.
- Fahrenheit's scale, 12.
 Farad, 21.
 Fats, 282.
 phosphorized, 282.
 Fatty compounds, 199, 201.
 Feldspar, 178, 180.
 Fermentation, 215.
 acetic, 215, 252.
 butyric, 216, 253.
 lactic, 216, 262.
 test, 249.
 Ferments, false, 216.
 true, 215.
 Ferric acetates, 136.
 chloride, 135.
 citrate, 136.
 ferrocyanide, 136.
 hydroxide, 134.
 with magnesium oxide, 115.
 oxide, 134.
 phosphate, 136.
 sulphates, 135.
 sulphide, 135.
 Ferroso-ferric oxide, 134.
 Ferrous acetate, 136.
 bicarbonate, 136.
 carbonate, 136.
 chloride, 135.
 ferricyanide, 137.
 hydroxide, 134.
 oxide, 134.
 phosphates, 136.
 sulphate, 135.
 sulphide, 134.
 Ferrum reductum, 133.
 Filtration, 67.
 Fire-damp, 203.
 Flavaniline, 372.
 Flowers, 17.
 Fluorene, 385.
 Fluoresceine, 349, 350.
 Fluorine, 73.
 Fluor spar, 73.
 Flux, black, 160.
 Force, 1.
 chemical, 48.
 electromotive, 20.
 Formal, 233.
 Formaldehyde, 228.
 Formaline, 228.
 Formals, 232.
 Formamide, 312.
 Formin, 319.
 Formonitrile, 303, 305.
 Formose, 229, 240.
 Formulæ, 32.
 algebraic, 193.
 empirical, 32.
 general, 193.
 graphic, 47, 193.
- Formulæ, rational, 46.
 typical, 47.
 Fossil resins, 385.
 wax, 204.
 Fowler's solution, 115.
 Freezing point, 11, 15.
 Fructose, 241.
 Fruit sugar, 241.
 Fucose, 237.
 Function, 36.
 Furazoles, 393.
 Furfural, 392.
 Furfuraldehyde, 392.
 Furfurane, 392.
 Furfurole, 392.
 reaction, 247.
 Furole, 392.
 Fusel oil, 220.
 Fusing point, 14.
 Fusion, 13.
 latent heat of, 14.
- Gadinin, 282.
 Galactose, 241.
 Galena, 138, 140.
 Gallisin, 240, 244.
 Gallium, 177.
 Galvanic battery, 19.
 cell, 19.
 circuit, 19.
 electricity, 18.
 Garnet, 178.
 Gas, carbonic acid, 272.
 laughing, 97.
 tar, 341.
 Gases, 4, 10, 15.
 absorption of, 11.
 Gasoline, 204.
 Gelatin, explosive, 247.
 sugar, 323.
 Geneva convention, 199.
 Germicides, 444.
 Glass of antimony, 122.
 soluble, 153.
 water, 153.
 Glauber's salt, 153.
 Glonoin, 280.
 Glucinium, 177.
 Glucosazone, 381.
 Glucose, 240.
 Glucoses, 237.
 Glucosides, 361.
 Glucosyl phenate, 361.
 Glucovanillin, 362.
 Glycerides, 280.
 Glycerine, 223.
 Glycerites, 224.
 Glycerol, 223.
 esters of organic acids, 281.
 halohydrines, 280.
 ketone, 237.
 trinitrate, 280.
 Glycerols, 222, 224.

- Glycine, 323.
Glycogen, 245.
Glycocoll, 323.
 trimethyl, 298.
Glycocolls, 322.
Glycol ethene, 222.
 ethylene, 222.
 halohydrines, 279.
 monothioethylene, 286.
 tetramethylethylene, 222.
Glycols, 221.
 xylylene, 352.
Glycolyl aldehyde, 237.
 urea, 395.
Glyoxal, 233, 262.
Glyoxaline, 396.
Glyoxyldiureide, 395.
Gold, 129.
 fulminating, 308.
 trichloride, 129.
Goulard's extract, 141.
Gram, calorie, 12.
 equivalent, 31, 37.
 molecule, 29.
Granulose, 245.
Grape sugar, 240.
Graphite, 125.
Gravity, specific, 3.
Grignard's compounds, 290.
 reactions, 290.
Groups, characterizing, 198.
Guaiacol, 347, 349.
Guanidine, 301.
Guanidines, substituted, 301.
Guanides, 405.
Guanine, 411.
Guaranine, 411.
Gum resins, 385.
Gums, 246.
Gun cotton, 247.
 powder, 158.
Guvacine, 422.
Gypsum, 169.

Halide anhydrides, 270.
Halides, acidyl, 270.
Halogens, 73.
Hausmannite, 131.
Heat, 11.
 changes in volume caused by, 12.
 effects of, 11.
 latent, 14.
 of fusion, 14.
 of vapor, 16.
 measure of, 12.
 quantity of, 11.
 specific, 17.
 units of, 62.
Heavy spar, 172.
Helium, 72.
Hematin, 273.
Hematite, 132.
Hematoporphyrin, 273.

Hemiterpenes, 382.
Hemochromogen, 273.
Hemoglobin, 273.
Heptoses, 236.
Heroïne, 434.
Heterocyclic compounds, 200, 334, 389, 414.
Heteroxanthine, 410.
Hexacarboyclic compounds, 336.
Hexadiene, 335.
Hexads, 30, 31.
Hexahydrobenzene, 335, 381.
Hexahydrocymene, 382.
Hexahydropyrazine, 400.
Hexahydropyridine, 398.
Hexamethylene, 335.
 tetramine, 319.
Hexatriene, 335.
Hexene, 335.
Hexites, 225.
Hexoses, 236, 237.
Histidin, 396.
Homatropine, 427.
Homologous series, 193.
Horn lead, 138.
Hydantoïn, 317, 395.
Hydracetine, 381.
Hydracids, 36.
Hydramines, 296, 319.
Hydrargyrum, 184.
Hydrates, 64.
Hydrazides, 302, 303.
Hydrazine, 96.
 compounds, 379.
Hydrazines, 302, 379.
 aromatic, 379.
Hydrazobenzene, 378, 379.
Hydrazo compounds, 378.
 nitrogen, 293.
Hydrazones, 377.
 aldehyde, 321.
 ketone, 321.
Hydrion, 35.
Hydroaromatic compounds, 381.
Hydrocarbons, 194, 201, 202.
 acetylene series, 201, 329.
 aliphatic, 201.
 condensed, 386.
 diacetylene, 201.
 diolefine, 330.
 ethene series, 327.
 hydroaromatic, 381.
 methane series, 201.
 monobenzenic, 341.
 olefine series, 327.
 saturated, 201.
Hydrocotarnine, 436, 438.
Hydrogen, 57.
 antimonide, 121.
 arsenide, 111, 115.
 bromide, 80.
 chloride, 76.
 cyanide, 303.

- Hydrogen, dioxide, 69.
 fluoride, 73.
 iodide, 82.
 nitride, 95.
 peroxide, 69.
 phosphides, 106.
 sulphide, 85.
 sulphuretted, 85.
 Hydrolysis, 33, 64.
 Hydronaphthalenes, 386.
 Hydropyridines, 398.
 Hydropyrimidines, 398.
 Hydropyrroles, 393.
 Hydroquinone, 349.
 Hydrosulphides, 87.
 Hydroterpenes, 382.
 Hydouracil, 401.
 Hydroxamines, 296, 319.
 Hydroxidion, 35.
 Hydroxides, 37, 64.
 alkyl, 211.
 basic, 64.
 hydrocarbon, 210.
 Hydroxyl, 37.
 determination of, 284.
 Hydroxylamine, 97.
 compounds, 292.
 aromatic, 370.
 Hyoscine, 427.
 Hyoscyamine, 426.
 Hypnone, 355.
 Hypophosphites, 108.
 Hypoxanthine, 411.

 Iceland spar, 170.
 Ichthyol, 287.
 Imide nitrogen, 293.
 Imido group, 293.
 Imidoparaffins, 293.
 Imides, 310, 313, 318.
 Imine bases, 292.
 Imine nitrogen, 293.
 Imines, 296, 313.
 Imino group, 293.
 Impenetrability, 2.
 Indene, 385.
 Indestructibility, 2.
 Indican, 363.
 urinary, 417.
 Indicanin, 363.
 Indiglucin, 363.
 Indigo blue, 417.
 white, 418.
 Indigotine, 417.
 Indium, 177.
 Indole, 415.
 homologues, 415.
 Indoxyl, 416.
 Induline dyes, 379.
 Induline, 241, 246.
 Inertia, 2.
 Inosite, 382.
 Insulators, 17.

 Inulin, 241, 246.
 Inversion, 241.
 Invertin, 361.
 Iodidion, 83.
 Iodides, 82.
 Iodine, 81.
 chlorides of, 83.
 number, Hübl's, 332.
 oxyacids of, 82.
 Iodoform, 207.
 Iodophenols, 348.
 Iodoquinine sulphate, 429.
 Ionization, 35.
 Ions, 17, 35.
 Iridium, 147.
 Iron, 132.
 acetates of, 136.
 chlorides of, 135.
 citrate of, 136.
 dialysed, 134.
 galvanized, 133.
 group, 130.
 hydroxides of, 134.
 magnetic oxide of, 134.
 oxides of, 134.
 phosphates of, 136.
 reduced, 133.
 spathic, 136.
 sulphates of, 135.
 sulphides of, 134.
 Ironstone, 132.
 Isatine, 417.
 Isoacetonitrile, 306.
 Isobenzonitrile, 306, 373.
 Isocholine, 296.
 Iso compounds, 202.
 Isocyanates, 307.
 Isocyanides, 295, 306.
 Isodipyridine, 424.
 Isodulcite, 237.
 Isoindole, 416.
 Isoleucine, 325.
 Isomaltose, 240, 244.
 Isomeres, optical, 239.
 Isomerism, 194, 337.
 place, 260, 337.
 position, 260.
 space, 238.
 stereo, 238.
 Isomorphism, 8.
 Isonitriles, 295.
 Isopropyl carbinol, 220.
 Isoquinoline, 419.
 alkaloids, 421, 433.
 Ivory black, 126.

 Jaborandine, 428.
 Jaborine, 428.
 Japaconine, 440.
 Japaconitine, 440.
 Javelle water, 158.
 Jervine, 441.

- Kaolin, 180.
 Kathode, 19.
 Kations, 20, 35, 45.
 Kelp, 81.
 Kermes mineral, 122.
 Kerosene, 204.
 Ketohydrazones, 380.
 Ketone acids, 266.
 dimethyl, 234.
 glycerol, 237.
 hydrazones, 321.
 phenylmethyl, 355.
 Ketones, 225, 233.
 aromatic, 354.
 hydroaromatic, 383.
 Ketopiperazines, 323.
 Ketopurines, 411.
 Ketoses, 236.
 Ketoximes, 320.
 Kilowatt, 41.
 King's yellow, 114.
 Knock-out-drops, 232.
 Krypton, 72.
- Labarraque's solution, 154.
 Labile substances, 49.
 Labradorite, 180.
 Lacmoid, 349.
 Lactam, methylguanidinacetic, 302.
 Lactams, 323.
 Lactides, 261, 283.
 Lactones, 261, 283.
 Lactose, 244.
 Lampblack, 126.
 Lapis infernalis, 165.
 Laughing gas, 97.
 Law or laws, Boyle-Mariotte, 10.
 Dalton-Gay Lussac, 13.
 of Ampère, 24.
 of Avogadro, 24.
 of Charles, 13.
 of definite proportions, 22.
 of Gay-Lussac, 24.
 of Graham, 58.
 of Henry, 11.
 of multiple proportions, 23.
 of reciprocal proportions, 23.
 Ohm's, 20.
 periodic, 54, 55.
- Lead, 138.
 acetates, 140.
 black, 125.
 carbonate, 141.
 chamber crystals, 99.
 chloride, 140.
 chromate, 140.
 dioxide, 139.
 group, 138.
 iodide, 140.
 monoxide, 139.
 nitrates, 140.
 oleate, 139.
 oxides, 139.
- Lead, oxychlorides, 140.
 red, 139.
 salts of, 140.
 subacetate, 141.
 sugar of, 140.
 sulphate, 140.
 sulphide, 140.
 white, 141.
- Leads, electric, 19.
 Lecithins, 282.
 Lethol, 279.
 Leucine, 325.
 Leucines, 325.
 Leucomaines, 442.
 Leucopararosaniline, 389.
 Levigation, 170.
 Levulose, 241.
 Lichenin, 246.
 Light, chemical effects of, 51.
 Lignin, 247.
 Lime, 168.
 chlorinated, 169.
 chloride of, 169.
 milk of, 169.
 quick, 168.
 slaked, 169.
 water, 169.
- Limestone, 170.
 Linkages, 196.
 Liquefaction, 16.
 Liqueurs, 219.
 Liquids, 4, 14, 15.
 diffusion of, 9.
- Liquor ammonii acetatis, 167.
 calcis, 169.
 chlori compositus, 75.
 hydrogenii dioxidi, 70.
 iodi compositus, 82.
 plumbi subacetatis, 141.
- Litharge, 139.
 Lithia water, 150.
 Lithium, 149.
 bicarbonate, 150.
 bromide, 149.
 carbonate, 150.
 chloride, 149.
- Loadstone, 134.
 Loganiaceæ, alkaloids of, 431.
 Lucifer disease, 106.
 Lugol's solution, 82.
 Lunar caustic, 165.
 Lutidines, 398.
 Lysidine, 299.
 Lysol, 347.
- Maclaurine, 360.
 Magma bismuthi, 143.
 Magnesia, 173.
 mixture, 109.
 Magnesite, 174.
 Magnesium, 173.
 carbonate, 174.
 chloride, 173.
 group, 172.

- Magnesium, hydroxide, 173.
 organic compounds, 289.
 oxide, 173.
 phosphates, 174.
 pyrophosphate, 174.
 sulphate, 173.
 Magnetic oxide, 134.
 Malachite, 181.
 Malonyldimethylurea, 404.
 Malonylguanide, 405.
 Malonylurea, 404.
 group, 403.
 Malt, 214.
 Maltose, 244.
 Manganates, 132.
 Manganese, 131.
 oxides, 131.
 salts, 132.
 Manganite, 131.
 Mannitan, 225.
 Mannite, 225.
 Mannitol, 225.
 Mannose, 240.
 Marble, 170.
 Marsh gas, 203.
 Martius' yellow, 387.
 Mass, action, 51.
 Massicot, 139.
 Matter, 1.
 general properties of, 2.
 states of, 4.
 Meconine, 436.
 Meerschaum, 173.
 Megohm, 21.
 Melampyrite, 225.
 Melecitose, 245.
 Melitose, 245.
 Membranes, permeable, 9.
 semipermeable, 10.
 Menthane, 383.
 Menthol, 383.
 Mercaptals, 286.
 Mercaptans, 285.
 Mercaptides, 285.
 Mercurammonium chloride, 188.
 Mercurdiammonium chloride, 188.
 Mercuric chloride, 187.
 cyanide, 188.
 fulminate, 308.
 iodide, 188.
 nitrate, 189.
 oxide, 185.
 sulphate, 189.
 Mercurous chloride, 186.
 iodide, 188.
 nitrate, 189.
 oxide, 185.
 sulphate, 189.
 Mercury, 184.
 ammoniated, 188.
 chlorides, 186.
 formamide, 312.
 fulminating, 308.
 iodides, 188.
 nitrates, 189.
 oxides, 185.
 phenate, 346.
 sulphates, 189.
 Meroquinene, 431.
 Mesitylene, 342.
 glycerol, 352.
 Meso compounds, 202.
 Mesoxalylurea, 266, 405.
 Metachloral, 231.
 Meta compounds, 338, 339.
 Metadiazine, 399.
 Metadioxybenzene, 349.
 Metaldehyde, 230.
 Metallo cyanides, 309.
 Metalloids, 51.
 Metals, 51, 53.
 noble, 102.
 Metamerism, 194.
 Metathesis, 33.
 Methanal, 228.
 Methane, 203.
 series, 201.
 triphenyl, 389.
 Methemoglobin, 273.
 Methene chloride, 206.
 Methenyl, chloride, 206.
 iodide, 207.
 Method, see Test.
 Methol, 279.
 Methoxybenzaldehyde, 354.
 Methoxyparaoxybenzaldehyde, 354.
 Methyl, amine, 295.
 acetanilide, 372.
 benzene, 342.
 bromide, 207.
 carbinol, 214.
 carbylamine, 306.
 chloride, 205.
 coniine, 422.
 cyanide, 306, 313.
 ethyl oxide, 267.
 glycocoll, 323, 324.
 guanidine, 301.
 hydride, 203.
 hydroxide, 214.
 indoles, 415, 416.
 iodide, 207.
 isocyanide, 306.
 isopropylcarbinol, 221.
 morphine, 434, 438.
 morphine methine, 438.
 oxalate, 387.
 oxide, 267.
 phenylhydrazine, 380.
 piperidine, 398.
 propylcarbinol, 221.
 pyridines, 398.
 quinine, 430.
 strychnium iodide, 432.
 uracils, 402.
 uramine, 301.

- Methyl, xanthines, 410.
Methylal, 233.
Methylene, chloride, 206.
Meunier's compounds, 291, 371.
Mica, 173, 178, 180.
Microhm, 21.
Milliampere, 21.
Mineral green, 183.
Minderus, spirit of, 167.
Minium, 139.
Mitis green, 183.
Mixture, 22.
Mixtures, isomorphous, 23.
 of solids, 23.
Mol, 29.
Molasses, 242.
Molecule, 24, 25.
Molecular theory, 24.
 volume, 29.
 weight, 26.
 determination of, 195.
Molybdenum, 128.
Monacetin, 223, 280.
Monads, 30, 31.
Monamides, 310.
 primary, 311.
 secondary, 311.
 tertiary, 311.
Monamines, 292.
 primary, 292.
 secondary, 294.
 tertiary, 295.
Monobenzenic compounds, 341.
 paraquinones, 351.
Monobromocamphor, 384.
Monochlormethyl chloride, 206.
Monoethylic sulphate, 277.
Monoglycerides, 223, 280.
Monoketones, 233, 354.
Monomorphyl sulphate, 434.
Mononitroparaffins, 292.
Monophenyl sulphate, 366.
Monosaccharides, 236.
Monoses, 236.
Monothioethylene glycol, 286.
Monsel's salt, 136.
Monureides, 316.
Morphine, 434, 438.
Morphium, 420.
Morrhuine, 282.
Mucilages, 246.
Murexide, 404.
Muscarin, 297.
Must, 218.
Mustard oils, 308, 333, 363.
Myazine compounds, 400.
Mydaleine, 300.
Myrosin, 333, 361.

Naphtha, 204.
Naphthalene, 386.
Naphthenes, 381.
Naphthol yellow, 387.

Naphthols, 386.
 substituted, 387.
Naphthoquinones, 387.
Narceine, 436, 438.
Narcotine, 436, 438.
Nascent state, 59.
Negative plate, 19.
 pole, 19.
Neon, 72.
Neuridine, 300.
Neurine, 297.
Neutral reaction, 33.
Nickel, 180.
 group, 180.
 sulphate, 180.
Nicotine, 423.
Niobium, 128.
Niton, 72.
Nitrates, 102.
Nitre, 157.
Nitrile bases, 292.
Nitriles, 303, 305.
 acid, 305.
 of carbonic acids, 307.
 of thiocarbonic acids, 307.
Nitrites, 101.
Nitro, 292.
 acids, 321, 370.
 alcohols, 319.
 aldehydes, 319.
 anisols, 369.
 benzenes, 367.
 benzol, 367.
 cellulose, 247.
 cresols, 370.
Nitrogen, 94.
 acids of, 100.
 amide, 293.
 amino, 293.
 azo, 293.
 bromide, 97.
 chloride, 97.
 diazo, 293.
 dioxide, 98.
 group, 93.
 halides, 97.
 hydrazo, 293.
 imide, 293.
 imino, 293.
 iodide, 97.
 monoxide, 97.
 nitrile, 293.
 oxides of, 97.
 pentoxide, 100.
 peroxide, 99.
 tetroxide, 99.
 trioxide, 99.
Nitroglycerin, 280.
Nitroketones, 319.
Nitroparaffins, 292.
Nitrophenetols, 369.
Nitrophenols, 369.
Nitrosenaphthols, 387.

- Nitrosophenols, 370.
 Nitrosyl bichloride, 102.
 chloride, 102.
 Nitrotoluenes, 368.
 Nomenclature, 42.
 of alcohols, 211, 221.
 of alkaloids, 420.
 of amines, 293.
 of carbon compounds, 198.
 Non-metals, 52.
 Nonoses, 236.
 Nordhausen oil of vitriol, 93.
 Normal compounds, 202.
 conditions, 4.
 Nortropan, 424.
 Nuclein bases, 409.
 Nucleus, 200.
 benzene, 334.

 Obtained substances, 208.
 Occlusion, 58.
 Octoses, 236.
 Ohm, 21.
 Oil, bone, 397.
 cod-liver, 282.
 fusel, 220.
 mustard, 333.
 of bitter almonds, 353.
 of Dippel, 397.
 of vitriol, 90.
 sperm, 282.
 Oils, drying, 282.
 fixed, 282.
 greasy, 282.
 lubricating, 204.
 mustard, 308.
 neutral, 282.
 non-drying, 282.
 semi-drying, 282.
 Ol, 211.
 Olefiant gas, 327, 328.
 Olefine, 327.
 acetylene series, 201.
 series, 201, 327.
 terpenes, 382.
 Olefines, 201.
 Oleoresins, 385.
 Open chain compounds, 199, 201.
 Opium alkaloids, 434, 437.
 Optical activity, 238.
 isomeres, 239.
 Organic compounds, 191, 192.
 Organo-halide compounds, 289.
 Organo-magnesium compounds, 289.
 Organo-metallic compounds, 288.
 Orientation, 337.
 Orpiment, 114.
 Ortho acids, 108.
 compounds, 338, 339.
 diazine, 399.
 dioxybenzene, 349.
 quinones, 350.
 Osazones, 236, 249, 380.

 Ose, 236.
 Osmium, 128.
 Osmosis, 9.
 Osmotic equivalent, 9.
 Otoliths, 170.
 Oxalylurea, 395.
 Oxazine, 399.
 Oxethylamine, 319.
 Oxhydril, 37.
 Oxidation, 60.
 Oxides, 61.
 basic, 61.
 indifferent, 61.
 neutral, 61.
 saline, 61.
 Oxime group, 301.
 Oxindole, 374, 417.
 Oxonium compounds, 289.
 Oxyacids, 36, 259.
 Oxyaldehydes, 228.
 Oxyamides, 322.
 Oxyamines, 296, 298, 319.
 Oxybenzaldehyde, 354.
 Oxycholine, 298.
 Oxycinchonine, 430.
 Oxycyanides, 228.
 Oxydimorphine, 434.
 Oxygen, 59.
 Oxygenium, 59, 60.
 Oxyhemoglobin, 273.
 Oxyhydrocymene, 383.
 Oxyindole, 416.
 Oxymorphine, 434.
 Oxynaphthalenes, 386.
 Oxyneurine, 298.
 Oxyphenylalanine, 374.
 Oxyphenylethylamine, 375.
 Oxypurines, 411.
 Oxysalts, 38.
 Ozocerite, 204.
 Ozone, 61.
 Ozonic ether, 70.

 Painter's colic, 141.
 Palladium, 147.
 Papaveraldine, 437.
 Papaverine, 436, 437.
 Para acetophenetidine, 373.
 Para compounds, 338, 339.
 coniine, 423.
 dioxybenzene, 349.
 Paraffin, 204.
 series, 201.
 Paraffins, 202.
 amido, 292.
 haloid derivatives of, 204.
 imido, 293.
 monohalogen, 205.
 nitro, 292.
 nitrogen derivatives of, 291.
 oxidation products of, 208.
 sulphur derivatives of, 285.
 Para formaldehyde, 228.

- Paraldehyde, 230.
Paramorphine, 436.
Paramylum, 246.
Para quinones, 351.
 triazine, 414.
 xanthine, 410.
Parchment paper, 247.
Paris green, 115, 183.
 yellow, 140.
Pearl ash, 159, 160.
Pentads, 30, 31.
Pentamethylenediamine, 299.
Pentene, 330.
Pentites, 225.
Pentoses, 236, 237.
Pentosides, 361.
Periodic law, 54, 55.
Perissads, 30.
Permanganates, 132.
Petrolatum, 204.
Petroleum, 204.
 ether, 204.
Phenacetine, 373.
Phenanthrene, 385.
 alkaloids, 422, 433.
Phenates, 346.
Phenetidines, 369, 373.
Phenetol, 361.
Phenol, 345.
 cymylic, 347.
 dyes, 350.
 esters, 347.
 methylisopropyl, 347, 348.
 phthaleïn, 350.
 sulphonates, 366.
 synthetic, 345.
Phenols, 344, 386.
 benzylic, 347.
 cresylic, 347.
 dihydric, 348.
 dimethyl, 347.
 diphenyl, 389.
 ethyl, 347.
 monohydric, 344.
 substituted, 348.
 trihydric, 350.
Phenones, 354.
Phenyl, 343.
 acetamide, 372.
 alanine, 374.
 amines, 371, 373.
 benzenes, 388.
 carbylamine, 373.
 dimethylpyrazolon, 394.
Phenylene, 343.
 diamines, 373, 380.
Phenyl glucosides, 361.
 glycocoll, 375.
 guanidine, 375.
 hydrazine, 379, 380, 381.
 test, 249.
 hydrazones, 380.
 hydroxide, 345.
Phenyl hydroxylamine, 370.
 isocyanide, 306.
 salicylate, 358.
 sulphide, 365.
 uracil, 402.
 urethanes, 314, 375.
Phloretin, 364.
Phloridzin, 364.
Phloroglucin, 350, 364.
Phlorose, 364.
Phosgene, 271.
Phosphates, 109.
Phosphine, 106.
Phosphines, 326.
Phosphorus, 103.
 acids of, 107.
 halides, 107.
 organic compounds of, 326.
 oxides, 107.
 oxychloride, 107.
 pentachloride, 107.
 pentoxide, 107.
 trichloride, 107.
 trioxide, 107.
Phthalamide, 373.
Phthaleïns, 350.
Phthalimide, 373.
Physical change, 1.
Physostigmine, 441.
Picolines, 398.
Pilocarpene, 428.
Pilocarpidine, 428.
Pilocarpine, 428.
Pinacone, 222.
Piperazine, 400.
Piperideïnes, 398.
Piperidine, 398, 423.
 alkaloids, 421, 422.
Piperidines, 398.
Piperine, 423.
Plaster of Paris, 170.
Platinic chloride, 148.
Platinum, 147.
 black, 147.
 group, 147.
 spongy, 147.
 tetrachloride, 148.
Plumbago, 125.
Plumbates, 140.
Plumbites, 139.
Pœonin, 350.
Poisons, 78, and see Toxicology.
Poles, electric, 19.
Polymerism, 194.
Polymerization, 229.
Polymethylenes, 335.
Polysaccharides, 236, 245.
Ponceau dyes, 387.
Populin, 364.
Porcelain, 218.
Porter, 218.
Positive plate, 19.
 pole, 19.

- Postulate, see Law.
 Potash, 156, 157, 160.
 Potassa, 156.
 Potassium, 156.
 acetate, 159.
 alcoholate, 217.
 alum, 179.
 arsenite, 115.
 bromate, 157.
 bromide, 157.
 carbonates, 159.
 chlorate, 158.
 chloride, 157.
 cyanates, 307.
 cyanide, 162.
 dichromate, 159.
 ethylate, 217.
 ferricyanide, 163.
 ferrocyanide, 162.
 hypochlorite, 158.
 hydrate, 156.
 hydroxide, 156.
 iodide, 157.
 myronate, 333.
 nitrate, 157.
 oxalates, 160.
 oxides, 156.
 permanganate, 159.
 phenate, 346.
 pyrosulphate, 159.
 sulphates, 158.
 sulphites, 159.
 tartrates, 160.
 Powder of Algaroth, 121.
 putty, 146.
 smokeless, 247.
 Precipitation, 67.
 Pressure, 4.
 critical, 15, 16.
 Preston salts, 167.
 Process (see also Reaction, Reagent, Test).
 ammonia, 155.
 Leblanc's 155.
 Solvay, 155.
 Proline, 393.
 Propanon, 234.
 Propantriol, 223.
 Propine, 330.
 Propyl carbinol, 220.
 hydroxide, 219.
 piperidine, 398, 422.
 Propylene, 330.
 Proteinochrome, 416.
 Proteinochromogen, 416.
 Prussian blue, 136, 163.
 Pseudo aconitine, 440.
 conhydrine, 422.
 morphine, 434.
 Ptomaines, 442.
 Purine, 406.
 bases, 409.
 compounds, 400.
 Purine group, 400, 405.
 Purpurin, 388.
 Putrefaction, 443.
 Putrescin, 299.
 Putty powder, 146.
 Pyrazine, 399.
 Pyrazolons, 394, 395.
 Pyridiazine, 399.
 Pyridine, 397.
 alkaloids, 421.
 bases, 397.
 homologues, 398.
 methylpyrrole, 424.
 Pyrimidine, 399.
 derivatives, 400.
 Pyrites, 84, 110, 132, 134.
 copper, 181.
 Pyrocatechin, 349.
 Pyrocatechol, 349.
 Pyrocomane, 398.
 Pyrodine, 381.
 Pyrogallol, 350.
 Pyrolusite, 131.
 Pyrone, 397.
 Pyroxam, 245.
 Pyroxylic spirit, 252.
 Pyroxylin, 247.
 soluble, 247.
 Pyrrazoles, 393.
 Pyrrole, 392, 424.
 Pyrrolidine, 393.
 alkaloids, 421.
 piperidine alkaloids, 421, 424.
 pyridine alkaloids, 421, 423.
 Pyrroline, 393.
 Pyrromonazoles, 393.
 Quaternary ammonium compounds, 295,
 296, 297, 298.
 hydroxides, 293.
 Quercite, 382.
 Quicklime, 168.
 Quicksilver, 185.
 Quina red, 360.
 Quinicine, 430.
 Quinidine, 430.
 Quinine, 429.
 hydrosulphate, 429.
 sulphate, 429.
 Quinol, 349.
 Quinoline, 419.
 alkaloids, 421, 428, 429.
 compounds, 418.
 Quinone, 351.
 Quinones, 350, 386, 387.
 Quinoxime, 370.
 Radicals, 45, 192.
 of acids, 46.
 Raffinose, 245.
 Reaction, 32 (see Process, Reagent, Test).
 Reactions, 33.

- Reagent, Fröhde's, 435.
 Marquis', 436.
 Nessler's, 96.
 Schiff's, 315.
Realgar, 114.
Reaumur's scale, 12.
Rectified spirit, 217.
Reduction, 58.
Refractory substances, 13.
Residues, 46.
Resins, 384.
Resistance, 20.
Resorcin, 349.
Resorcinol, 349.
 phthaleïn, 350.
Reversible reactions, 50.
Rhamnose, 237.
Rhigolene, 204.
Rhodium, 147.
Ribose, 237.
Rings, 200.
Roburite, 368.
Rochelle salt, 162.
Rock crystal, 127.
Rosin, 382.
Rubidium, 163.
Ruby, 178, 181.
Ruthenium, 147.
- Sabadilline, 441.
Saccharates, 238, 241, 243.
Saccharin, 366.
Saccharobioses, 236, 241.
Saccharose, 242.
Saccharotrioses, 236.
Saccharum lactis, 244.
Sal ammoniac, 166.
Salacetol, 358.
Salæratius, 160.
Salicin, 364.
Salicyl hydride, 354.
Salicylal, 354.
Salicylide, 364.
Saligenin, 352.
Salipyrine, 394.
Salol, 358.
Sal soda 155.
Salt, 152.
 of lemon, 160.
 of Saturn, 140.
 of sorrel, 160.
 of tartar, 159, 160.
 rock, 152.
 sea, 152.
 soda, 155.
 table, 152.
Saltpeter, 157.
 Chile, 152.
 cubic, 152.
Salts, 36, 38, 39.
 acid, 38, 45.
 basic, 38, 45.
 double, 45.
- Salts, haloid, 38.
 modified, 397.
 neutral, 45.
 normal, 45.
Sal volatile, 167.
Sanguinarine, 397.
Santonin, 364.
Saponification, 276.
Sapphire, 178.
Saprine, 300.
Sarcosine, 324.
Sarkine, 411.
Saturated compounds, 196, 201.
Scandium, 177.
Scheele's green, 115, 183.
Schweinfurth green, 115, 183.
Scopolamine, 427.
Scopoline, 427.
Seidlitz salt, 173.
Selenite, 169.
Selenium, 93.
Selenmonazole, 393.
Series, electrochemical, 34.
Silex, 127.
Silica, 127.
Silicates, 127.
Silicium, 127.
Silicon, 127.
 carbide, 127.
 chloride, 127.
 dioxide, 127.
- Silver, 164.
 acetylide, 329.
 bromide, 165.
 chloride, 165.
 fulminate, 308.
 german, 180.
 iodide, 165.
 monoxide, 164.
 nitrate, 165.
 oxides, 164.
- Skatole, 416.
Smokeless powder, 247, 280,
Soaps, 282.
Soapstone, 173.
Soda, 155.
 baking, 156, 161.
 blackball, 155.
 caustic, 155.
 crystals, 155.
 lye, 152.
 salt, 155.
 washing, 155.
 water, 272.
- Sodium, 151.
 acetate, 155.
 acetylide, 329.
 alcoholate, 217.
 arsenates, 154.
 arsenites, 115, 154.
 bicarbonate, 156.
 borate, 154.
 bromide, 152.

- Sodium carbonates, 155.
chlorate, 154.
chloride, 152.
dioxide, 151.
ethylate, 217.
group, 149.
hydroxide, 151.
hypochlorite, 154.
hyposulphite, 153.
iodide, 152.
metaphosphate, 154.
monoxide, 151.
nitrate, 152.
nitroprusside, 310.
oxides, 151.
permanganate, 155.
phosphates, 153.
pyroborate, 154.
pyrophosphate, 154.
sesquicarbonate, 156.
silicates, 153.
sulphates, 152.
sulphite, 153.
sulphovinate, 277.
thiosulphate, 153.
tungstate, 128.
- Solanidin, 364.
Solanin, 364.
Solids, 4.
Solute, 14.
Solution—Solutions, 14.
chemical, 14.
concentration of, 37.
decinormal, 38.
dilute 14, 15.
equivalent normal, 38.
molecular normal, 37.
normal, 37.
percentage, 37.
physical, 14.
physiological salt, 152.
salt, 152.
saturated, 15.
simple, 14.
solid, 23.
standard, 38.
strength of, 37.
supersaturated, 15.
unsaturated, 15.
- Solubilities, table of, 446, 447.
Solubility, 14.
Solvay process, 155.
Solvent, 14.
Somnal, 314.
Sorbinoose, 241.
Sorbite, 225.
Sorbitol, 225.
Space isomerism, 238.
Spasмотoxine, 443.
Specific heat, 17.
volume, 4.
weight, 3.
Spermaceti, 279.
- Spirit, methylated, 214.
neutral, 219.
potato, 220.
proof, 218.
pyroxylic, 214, 252.
wood, 214.
- Spirits, 216, 219.
of Minderus, 167.
of wine, 214.
- Spiritus rectificatus, 217.
- Stability, 48.
- Stable substances, 49.
- Stannates, 146.
- Stannic chloride, 146.
oxide, 146.
- Stannous chloride, 146.
hydroxide, 146.
oxide, 146.
- Starch, 245.
animal, 245.
cellulose, 245.
hydrated, 245.
paste, 245.
soluble, 245.
- States of matter, 4.
- Steel, 133.
- Stereochemistry, 238.
- Stereoisomerism, 238.
- Stethol, 279.
- Stibine, 121.
- Stibines, 326.
- Stilbene, 389.
- Stoichiometry, 41.
- Storax, 352.
- Strontianite, 171.
- Strontium, 171.
- Strychnidene, 432.
- Strychnine, 431.
- Strychnos alkaloids, 431.
- Styracol, 349.
- Sublimate, corrosive, 187.
- Sublimation, 17.
- Subsidence, 68.
- Substance, 1.
- Substitution, 196.
- Succinyl morphine, 434.
- Sucrates, 243.
- Sugar, beet, 243.
barley, 243.
burnt, 243.
candy, 243.
cane, 242.
diabetic, 240.
fruit, 241.
gelatin, 323.
grape, 240.
invert, 241, 243.
liver, 240.
maple, 243.
milk, 244.
muscovado, 242.
of lead, 140.
raw, 242.

- Sulphates, 92.
Sulphethylates, 277.
Sulphides, 87, 284.
Sulphites, 89.
Sulpho, 85.
Sulphocarbulates, 366.
Sulphonals, 287.
Sulphonation, 365.
Sulphones, 284, 286, 366.
 of thioaldehydes, 286.
Sulphosion, 89.
Sulphurylechloride, 88.
Sulphovinates, 277.
Sulphoxides, 284, 286.
Sulphur, 84.
 aromatic derivatives of, 365.
 dioxide, 87.
 flowers of, 84.
 group, 83.
 milk of, 84.
 oxides, 87.
 oxyacids of, 89.
 plastic, 84.
 precipitated, 84.
 roll, 84.
 sublimed, 84.
 trioxide, 88.
Sultones, 387.
Symbols, 31.
Symmetrical positions, 338.
Synthesis, 33, 63.

Talc, 173.
Tannins, 360.
Tantalum, 128.
Tartar, cream of, 161.
 crude, 161.
 emetic, 162.
 salt of, 159, 160.
 soluble, 160.
Tartrates, 160.
Tartronylurea, 404.
Tellurium, 93.
Temperature, 11.
 absolute, 13.
 critical, 15.
Terpenes, 382.
Terpin hydrate, 383.
Terpins, 383.
Terra alba, 170.
Test (Process, Reaction).
 Almèn, 249.
 Anderson, 397.
 bismuth reduction, 249.
 biuret, 315, 318.
 Boettger, 249.
 copper reduction, 248.
 Fehling, 248.
 fermentation, 249.
 Fischer, 249.
 furfurole, 247.
 Gallois, 383.
 Hoffman, 295, 375.

Test, Hofmeister, 326.
 Husemann, 436.
 indophenol, 372.
 Kjeldahl, 195.
 Kossel, 411.
 Marsh, 118.
 Mulder-Neubauer, 418.
 murexide, 408.
 Nessler, 96.
 Nylander, 249.
 osazone, 249.
 Pavy, 248.
 Pellagri, 435.
 phenylhydrazine, 249.
 pine-shaving, 346, 392, 393, 416.
 Piria, 375.
 pyrrole, 416.
 Reinsch, 117.
 Riegler, 249.
 Scherer, 326, 375, 383.
 Tollens, 247.
 Trommer, 248.
 Wiedel, 402.

Tetanine, 443.
Tetanotoxine, 443.
Tetrads, 30, 31.
Tetra hydrobenzenes, 335.
 hydrodiphenyl, 388.
 hydronaphthols, 387.
 hydropyridine alkaloids, 421.
 hydropyridines, 398.
 hydropyrrole, 393.
 hydrostrychnine, 432.
 ketohexahydropyrimidine, 405.
 ketones, 235.
 methyllumonium hydroxide, 295.
 methylenediamine, 299.
 methylethylene glycol, 222.
 methyleneimine, 393.

Tetronal, 287.
Tetroses, 236, 237.
Thallium, 168.
Thebaine, 436, 439.
Thebaol, 439.
Theïne, 411.
Theobromine, 410.
Theophylline, 410.
Theory, atomic, 24.
 molecular, 24.
Therm, 12.
Thermal capacity, 17.
 unit, 12.
Thermometers, 11.
Thiazine, 399.
Thio, 85.
 acetals, 286.
 acids, 284, 287.
 alcohols, 284, 285.
 aldehydes, 284, 286.
 anhydrides, 87, 287.
 antimonates, 122.
 antimonites, 122.
 aromatic compounds, 365.

- Thio azoles, 393.
 bases, 37.
 Thiocol, 349.
 Thio ethers, 284, 285.
 ethylates, 285.
 glycols, 285.
 ketones, 284.
 Thiophene, 392.
 Thiophenol, 365.
 Thiourea, 316.
 Thymine, 402.
 Thymol, 347.
 Tin, 145,
 chlorides, 146.
 crystals, 146.
 foil, 146.
 group, 144.
 hydrates, 146.
 oxides, 146.
 plates, 146.
 Tinstone, 146.
 Tinctures, 216.
 Titanium, 144.
 Toluene, 342.
 sulphamide, 366.
 sulphonic chlorides, 366.
 Toluidines, 372.
 Toluol, 342.
 Toluyll benzene, 388.
 Toluylene, 389.
 Tolypyrine, 395.
 Topaz, 178.
 Toxalbumins, 443.
 Toxicology, 78, 116, and see Poisons,
 Corrosives.
 aconite, 440.
 aldehyde, 230.
 ammonia, 167.
 aniline, 371.
 antimony, 123.
 arsenic, 115.
 atropine, 426.
 barium, 172.
 bismuth, 144.
 carbolic acid, 346.
 carbon dioxide, 274.
 carbon disulphide, 288.
 carbon monoxide, 271.
 chloral hydrate, 232.
 chloroform, 207.
 copper, 184.
 cyanides, 304.
 digitalis, 363.
 hydrogen sulphide, 86.
 illuminating gas, 271.
 iodine, 82.
 lead, 141.
 mercury, 189.
 mineral acids, 78.
 nicotine, 424.
 nitric acid, 103.
 nitrobenzene, 368.
 nitrogen tetroxide, 100.
 opium, 439.
 Toxicology, oxalic acid, 258.
 phenol, 346.
 phosphorous, 105.
 potassium, 163.
 silver, 165.
 sodium, 163.
 strychnine, 433.
 sulphuric acid, 92.
 zinc, 177.
 Toxines, 443.
 Transposition, 33.
 Transterpene, 383.
 Triacetin, 223, 280.
 Triacetoneamine, 319.
 Triads, 30, 31.
 Triamides, 310.
 Triamines, 292.
 Triazines, 413.
 Tribrommethane, 207.
 Tributyrin, 281.
 Tricaprin, 281.
 Tricaproin, 281.
 Tricaprylin, 281.
 Trichlor aldehyde, 230.
 methane, 206.
 Tricyanogen chloride, 304.
 Tryglycerides, 223, 280.
 Triiodomethane, 207.
 Triketones, 235, 354.
 Triketohexahydropyrimidine, 404.
 Triketopurine, 406.
 Triketotetrahydroglyoxaline, 395.
 Trimargarin, 281.
 Trimethylamine, 295.
 Trimethylcarbinol, 220.
 Trimethylethylene, 330.
 Trimethylene diamine, 299.
 Trimethyloxethylammonium hydroxide,
 296.
 Trimethyloxethylideneammonium hy-
 droxide, 296.
 Trimethylvinylammonium hydroxide,
 297.
 Trimorphism, 8.
 Trinitroglycerol, 280.
 Trinitrophenols, 369.
 Triolein, 281.
 Triols, 223.
 Trional, 287.
 Trioses, 236, 237.
 Trioxanthraquinone, 388.
 Trioxycyanidine, 307.
 Trioxymethylene, 228.
 Tripalmitin, 281.
 Triphenylbenzene, 388.
 Triphenylmethane, 389.
 Triple phosphate, 174.
 Trisaccharides, 236, 245.
 Tristearin, 281.
 Tropan alcohol, 425.
 alkaloids, 421, 424.
 Tropeïnes, 427.
 Tropeolins, 387.
 Tropidine, 425.

- Tropine, 398, 425.
 atropate, 427.
 tropate, 425.
Tryptophane, 416.
Tungsten, 128.
Turnbull's blue, 137, 163.
Turner's yellow, 140.
Turpentine, 382.
Turpeth mineral, 189.
Tutty, 176.
Tyrosine, 374.
- Unsaturated compounds, 197.
Unsymmetrical positions, 338.
Uracil, 401.
 group, 400, 401.
Uralium, 314.
Uranium, 137.
Uranyl, 138.
Urates, 408.
 nitrate, 138.
Urea, 314.
 nitrate, 315.
 oxalate, 315.
Ureas, compound, 316.
Ureïdes, 316.
 diacidyl, 317.
 mixed, 317.
 monacidyl, 317.
Urethanes, 313.
Urotropin, 319.
Uroxanthine, 417.
- Valence, 30.
Valerene, 330.
Vanadium, 128.
Vanillin, 354.
Vapor, 15, 16.
 latent heat of, 16.
Vaporization, 15.
Varech, 81.
Vaseline, 204.
Veratrine, 441.
Veratrol, 349.
Verdigris, 183.
Veronal, 404.
Verona yellow, 140.
Vichy salt, 156.
Vicinal positions, 338.
Vinegar, 252.
 wood, 252.
Vitriol, blue, 183.
 green, 135.
 oil of, 90.
 white, 176.
Volt, 21.
Volume, specific, 4.
- Water, 62.
 baryta, 172.
 chlorine, 75.
 in the body, 69.
 lime, 169.
 lithia, 150.
- Water, maximum density of, 13.
 of constitution, 64.
 of crystallization, 8, 63, 64.
 oxygenated, 69.
 soda, 272.
- Waters, bitter, 174.
 chlorides in, 65.
 hardness of, 66.
 impurities in, 65.
 lead in, 67.
 mineral, 68.
 natural, 64.
 nitrogen in, 66, 67.
 organic matters in, 66.
 poisonous metals in, 67.
 potable, 64, 65.
 purification of, 67, 68.
 solids in, 65.
- Watt, 21.
Wax, 204.
Weight, 2.
 absolute, 3.
 apparent, 3.
 atomic, 26.
 equivalent, 31.
 molecular, 26, 195.
 relative, 3.
 specific, 3.
- White lead, 138, 141.
 precipitate, 188.
- Wines, 218.
Witherite, 172.
Wort, 215.
- Xanthine, 410.
 bases, 409.
Xanthone, 358.
Xenols, 347.
Xenon, 72.
Xylenes, 342.
Xylenols, 347.
Xylidines, 372.
Xylodin, 245.
Xylols, 342.
Xylose, 237.
Xylyleneglycols, 352.
- Yeast, 215.
Yellow wash, 186.
- Zero, absolute, 13.
Zinc, 175.
 alkyls, 288.
 butter of, 176.
 carbonate, 176.
 chloride, 176.
 ethide, 288.
 ethyl, 288.
 hydroxide, 176.
 methide, 288.
 methyl, 288.
 oxide, 176.
 sulphate, 176.
- Zirconia, 145.
Zirconium, 145.



ELEMENTS

NAME	Symbol	Atomic Weight		NAME	Symbol	Atomic Weight	
		Approximate	International (1918) O=16			Approximate	International (1918) O=16
Aluminium	Al	27	27.1	Molybdenum	Mo	96	96.0
Antimony (<i>Stibium</i>)	Sb	120	120.2	Neodymium	Nd	144	144.3
Argon	A	40	39.88	Neon	Ne	20	20.2
Arsenic	As	75	74.96	Nickel	Ni	58	58.68
Barium	Ba	137	137.37	Niton (Radium Emanation) . . .	Nt	222	222.4
Bismuth	Bi	208	208.00	Nitrogen	N	14	14.01
Boron	B	11	11.0	Osmium	Os	191	190.9
Bromine	Br	80	79.92	Oxygen	O	16	16.00
Cadmium	Cd	112	112.40	Palladium	Pd	107	106.7
Cæsium	Cs	133	132.81	Phosphorus	P	31	31.04
Calcium	Ca	40	40.07	Platinum	Pt	195	195.2
Carbon	C	12	12.005	Potassium			
Cerium	Ce	140	140.25	(<i>Kalium</i>)	K	39	39.10
Chlorine	Cl	35.5	35.46	Praseodymium (<i>c</i>)	Pr	141	140.9
Chromium	Cr	52	52.0	Radium	Ra	226	226.0
Cobalt	Co	59	58.97	Rhodium	Rh	103	102.9
Columbium (<i>a</i>) . . .	Cb	93	93.1	Rubidium	Rb	85	85.45
Copper (<i>Cuprum</i>)	Cu	63	63.57	Ruthenium	Ru	102	101.7
Dysprosium	Dy	162	162.5	Samarium	Sa	150	150.4
Erbium	Er	168	167.7	Scandium	Sc	44	44.1
Europium	Eu	152	152.0	Selenium	Se	79	79.2
Fluorine	F	19	19.0	Silicon	Si	28	28.3
Gadolinium	Gd	157	157.3	Silver (<i>Argentum</i>)	Ag	108	107.88
Gallium	Ga	70	69.9	Sodium (<i>Natrium</i>)	Na	23	23.00
Germanium	Ge	72	72.5	Strontium	Sr	87.5	87.63
Glucinum (<i>b</i>) . . .	Gl	9	9.1	Sulphur	S	32	32.06
Gold (<i>Aurum</i>) . .	Au	197	197.2	Tantalum	Ta	181	181.5
Helium	He	4	4.00	Tellurium	Te	127	127.5
Holmium	Ho	163	163.5	Terbium	Tb	159	159.2
Hydrogen	H	1	1.008	Thallium	Tl	204	204.0
Indium	In	115	114.8	Thorium	Th	232	232.4
Iodine	I	127	126.92	Thulium	Tm	168	168.5
Iridium	Ir	193	193.1	Tin (<i>Stannum</i>) . . .	Sn	118.5	118.7
Iron (<i>Ferrum</i>) . .	Fe	56	55.84	Titanium	Ti	48	48.1
Krypton	Kr	83	82.92	Tungsten			
Lanthanum	La	139	139.0	(<i>Wolframium</i>) .	W	184	184.0
Lead (<i>Plumbum</i>) .	Pb	207	207.20	Uranium	U	238	238.2
Lithium	Li	7	6.94	Vanadium	V	51	51.0
Lutecium	Lu	175	175.0	Xenon	Xe	130	130.2
Magnesium	Mg	24	24.32	Ytterbium (<i>d</i>) . .	Yb	173	173.5
Manganese	Mn	55	54.93	Yttrium	Yt	89	88.7
Mercury				Zinc	Zn	65	65.37
(<i>Hydrargyrum</i>)	Hg	200	200.6	Zirconium	Zr	90	90.6

- (a) Also formerly known as Niobium, Nb.
 (b) Also formerly known as Beryllium, Be.
 (c) Also formerly known as Didymium, Di.
 (d) Also known as Neoytterbium.

TABLE TO ILLUSTRATE THE PERIODIC SYSTEM.

Series	ZERO GROUP — —	GROUP I — R ₂ O	GROUP II — RO	GROUP III — R ₂ O ₃	GROUP IV RH ₄ RO ₂	GROUP V RH ₃ R ₂ O ₅	GROUP VI RH ₂ RO ₃	GROUP VII RH R ₂ O ₇	GROUP VIII — RO ₄ ?
1	—	H=1	—	—	—	—	—	—	—
2	He=4	Li=7	Gl=9	B=11	C=12	N=14	O=16	F=19	—
3	Ne=20	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35.5	—
4	A=40	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Ni=58 Co=59
5	—	Cu=63	Zn=65	Ga=70	Ge=72	As=75	Se=79	Br=80	—
6	Kr=83	Rb=85	Sr=87	Yt=89	Zr=90	Cb=93	Mo=96	—	Ru=101 Rh=103 Pd=106
7	—	Ag=108	Cd=112	In=114	Sn=119	Sb=120	Te=127	I=127	—
8	Xe=130	Cs=133	Ba=137	La=139	Ce=140	Nd=144	Tb=159	—	—
9	—	—	—	—	—	Er=167	—	—	—
10	—	—	—	Yb=173	—	Ta=181	W=184	—	Os=191 Ir=193 Pt=195
11	—	Au=197	Hg=200	Tl=204	Pb=207	Bi=208	—	—	—
12	Nt=222	—	Ra=226	—	Th=232	—	U=238	—	—

The figures used as atomic weights are approximate.
For table of International Atomic Weights (1918), see page 27.

